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Thermal behaviour of Fe-doped silicate–phosphate glasses

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Abstract Thermal behaviour and structure of glasses from the SiO_2–P_2O_5–K_2O–MgO–CaO system modified by Fe_2O_3 addition were studied by DSC, XRD and FTIR methods. It has been found that the replacement of MgO and CaO modifiers by Fe_2O_3 in the structural network of silicate–phosphate glass results in decrease of the glass transition temperature (T_g) and heat capacity change (ΔC_p) accompanying the glass transformation. Simultaneously, the ability for crystallization, its course and the type of the forming phases depend on the relative proportions between iron and phosphorus as components forming the silicate–phosphate structure. The type of the crystal phases forming in the course of heating the considered glass has been found to be in agreement with the character of the domains occurring in this glass, confirmed by FTIR examinations.

Keywords Glass transition · Heat capacity · Crystallization · Silicate–phosphate glasses

Introduction

Iron is usually considered as a component which colours glass influencing its optical properties [1]. The ability of glasses containing iron in their structure to absorb the UV and IR radiation was used to produce light filters and different types of protective glasses. Progress in studies of glass is manifested by the development of new glasses with unconventional properties. Amongst them, glasses containing biogenic elements (macroelements—P, Ca, Mg, K and microelements—B, Cu, Fe, Zn) in their composition, which release the form that is available for plants in the soil biological environment, should be mentioned. This type of silicate–phosphate glasses (SiO_2 (>27 wt%)–P_2O_5 (0–15 wt%)–K_2O (0–20 wt%)–MgO (15–30 wt%)–CaO (10–20 wt%) plus microelements (1–10 wt%) [2]) can be used in practice as ecological fertilizers providing a controlled release rate of the nutrients for plants [3]. In this type of glasses iron plays an important role as a microelement. Its influence in the growth process of plants is connected with energy transformation indispensable in photosynthesis, regulation of ox–redox reactions and participation in nucleic acids metabolism.

Chemical activity of such glasses in the soil environment strongly depends on the type and amount of components of the glass network and the positions they occupy in it. Introduction of Fe_2O_3 to such glasses decreases their solubility in conditions simulating the soil environment [4].

Thermal behaviour of silicate–phosphate glasses modified by addition of CaO and MgO was studied in [5, 6] by DSC, XRD and FTIR methods.

This article deals with the synthesis and study of the effect of Fe_2O_3 on the thermal behaviour of two groups of glasses from the SiO_2–P_2O_5–K_2O–MgO–CaO system.

Experimental

Glasses from the SiO_2–P_2O_5–CaO–MgO–K_2O system modified with Fe_2O_3 addition were obtained by the melting a mixture of pure materials, i.e. SiO_2, H_3PO_4, K_2CO_3, MgO, $CaCO_3$ and Fe_2O_3 in platinum crucibles, in the temperature at 1,450 °C and fast cooling of the melt in water. The obtained amorphous material was grinded to the

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grain size 0.1–0.3 mm. The chemical composition of examined glasses is presented in Table 1.

DSC curves were carried out using Netzsch STA 449 F3 Jupiter analyser. Glass samples (60 mg) were heated in platinum crucibles, in nitrogen atmosphere, at a rate of 10 °C min^{-1} to the temperature of 1,100 °C.

The glass transformation temperature T_g was determined as the midpoint of the change in C_p in the glass transformation region, and the values of crystallization temperature T_c were determined as the onset of the first crystallization peak. Changes of ΔC_p at the T_g point and enthalpy of crystallization effects were determined applying Netzsch Proteus Thermal Analysis—Version 5.0.0.

To identify the crystal phases created during isothermal process of glass heating, in temperatures inferred from the DSC measurements XRD method (X'Pert PRO Diffractometer) was applied.

FTIR spectra (Digilab FTS 60v spectrometer) were collected after 256 scans at 4 cm^{-1} resolution. Samples were prepared by the standard KBr pellets method. Spectra decomposition has been carried out according to the mathematical self-deconvolution method using the minimization of the number of the bands rule, proposed by Handke et al. [7].

Results and discussion

Glass transformation

DSC curves for two groups of glass compositions are shown in Fig. 1, which exhibit an endothermal peak due to the glass transformation followed by an exothermal one due to crystallization. The glass transformation characteristics are shown in Table 2.

The gradual increase of iron amount in the structure of glass at the cost of decreasing content of calcium and magnesium, with the constant MgO/CaO ratio, results in a gradual decrease of the glass transformation temperature T_g. Decrease in the value of T_g correlates with the decrease of ΔC_p accompanying the glass transformation. It can be noted that in the low phosphate content glasses, the changes of T_g and ΔC_p are less rapid than in the glasses containing 6 mol% P_2O_5 (Table 2).

Table 1 Chemical composition of silicate–phosphate glasses/mol%

Glass	SiO_2	P_2O_5	K_2O	MgO	CaO	Fe_2O_3
02Fe2P	43.0	2.0	6.0	28.8	20.0	0.2
2Fe2P	43.0	2.0	6.0	27.7	19.3	2.0
4Fe2P	43.0	2.0	6.0	26.5	18.5	4.0
02Fe6P	41.0	6.0	6.0	27.5	19.3	0.2
2Fe6P	41.0	6.0	6.0	26.2	18.8	2.0
4Fe6P	41.0	6.0	6.0	25.3	17.7	4.0

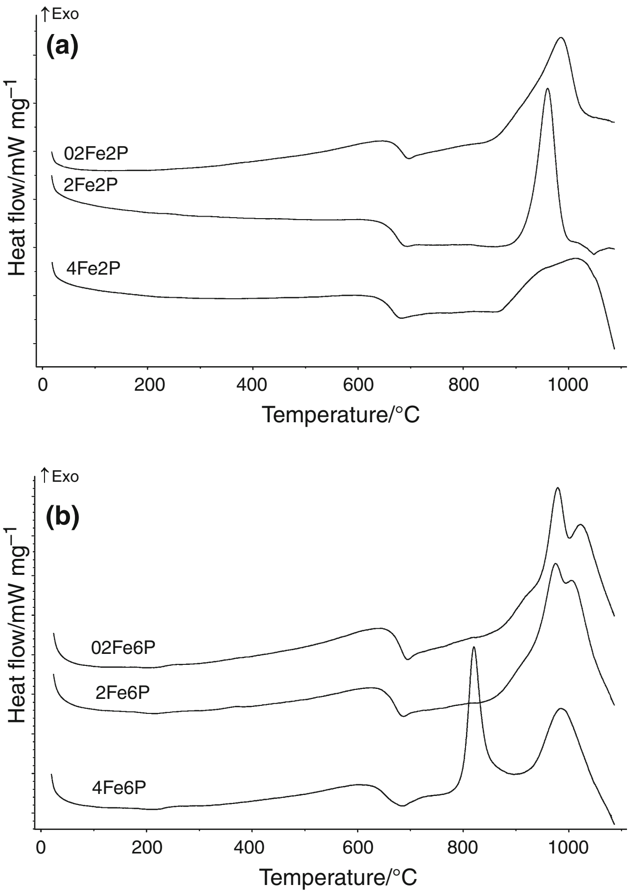

Fig. 1 DSC curves of analysed silicate–phosphate glasses

Table 2 Thermal characteristics of glass transformation effect of Fe-doped glasses

Glass	T_g/°C	ΔC_p/J g^{-1} K^{-1}
02Fe2P	675	0.57
2Fe2P	669	0.54
4Fe2P	657	0.53
02Fe6P	676	0.50
2Fe6P	662	0.50
4Fe6P	648	0.38

The changes of the values of T_g and ΔC_p are induced by the relaxation of stresses occurring in the glass disordered structure through breaking of oxygen bonds of the considered glass network [8].

In this study the ionicity (i_G) value of bonds of the components atoms with oxygen according to Görlich's scale [9] has been applied as a parameter characterizing the strength of bonds. The less ionic character of Fe^{III}–O bonds ($i_G = 0.529$) in comparison with Ca–O bonds ($i_G = 0.707$) and Mg–O bonds ($i_G = 0.670$) is responsible for the appearance of structural strains which make the bonds breakable. That is why, together with the increase of the iron amount in the structure of considered glasses, the relaxation of arising stresses by the chemical bonds' breaking requires a smaller amount of energy, hence smaller T_g values, which correlate with ΔC_p change.

Effect of iron on the glass structure of examined glasses is evidenced by FTIR spectra (Fig. 2). FTIR study shows that introduction of increasing content of iron into the structure of glasses belonging to the SiO_2–P_2O_5–K_2O–CaO–MgO system containing both small and large phosphorus amounts causes shifts in band positions towards lower wavenumbers, showing a depolymerization effect of iron on the glass network. It should be noted that with increasing content of iron in the glass structure only the bands at 700–800 cm^{-1} show the tendency to shift towards higher wavenumbers. These bands originate from the combination of vibrations of Si–O–Si, Si–O–P and P–O–P bridges. The bands shift may be explained by the increase in covalent character and strengthened P–O–P bonds as more iron content is introduced into the silicate–phosphate glass network.

It was also found that along with the iron increase in glasses containing 6 mol% P_2O_5, separation of absorption bands occurs. They are assigned to the combination of bending vibrations of O–Si–O and O–P–O bonds.

The observations suggest that same changes around the P–O–P bonds in the structure of considered glasses take place.

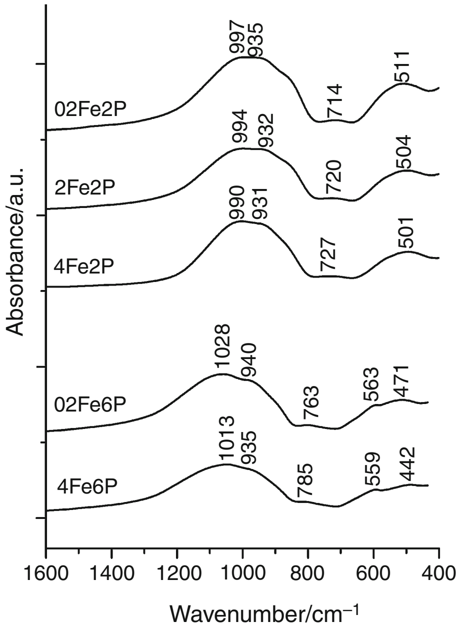

Fig. 2 FTIR spectra of analysed silicate–phosphate glasses

Crystallization

The effects of iron and phosphorus content on the parameters characterizing crystallization of examined glasses are summarized in Table 3.

The DSC studies showed a small thermal stability of the low phosphate content glasses (2 mol%) with the introduction of small iron amount as manifested by small thermal stability parameter ΔT (Table 3). Simultaneously, tenfold iron amount increase in the structure of these glasses (2 mol% Fe_2O_3) causes the increase of their thermal stability, whilst further iron amount increase again results in reducing its thermal stability.

An opposite tendency was found in the high phosphate content glasses (6 mol%). Decrease of their thermal stability parameter with the introduction of increasing iron amount reflects their increasing ability for crystallization. At the same time gradual increase of iron content results in a gradual decrease of the crystallization temperatures (T_c) and increase of corresponding crystallization enthalpies (ΔH_c).

The changing shape of DSC crystallization peaks (Fig. 1) indicates that iron introduction into the both (low and high phosphorus content) glasses changes the course of their crystallization. For 02Fe2P glass, single-step crystallization occurs at lower temperature of 891 °C, in a broad temperature range. XRD analysis showed that by heating this type of glass, crystalline $CaMgSiO_4$ as a main phase is formed. Silicates of the akermanite ($Ca_2MgSi_2O_7$) and forsterite (Mg_2SiO_4) types are identified by XRD, as the additional crystallization products. The 2Fe2P glass is also characterized by a single crystallization step, but it takes place at a higher temperature, in a significantly narrow temperature range and is well marked. The calcium–magnesium–iron silicate of $Ca(Mg_{0.93}Fe_{0.07})SiO_4$ composition turned out to be a main crystallization product of this glass. The glass containing 4 mol% of Fe_2O_3 crystallizes in one step, but it takes place in a broad temperature range and is characterized by significantly higher ΔH_c. The XRD analysis of the glass annealed at 1,000 °C (Fig. 3) found the presence of complex silicate of $Ca_{1.003}[Mg_{0.895}Fe_{0.105}]((Si_{1.901}Fe_{0.1})O_6)$ composition. As the additional crystallization product the silicate of the forsterite type was identified.

In the case of glasses containing 6 mol% of P_2O_5 the crystallization is a multistage process. The crystallization of 02Fe6P and 2Fe6P glasses is manifested on the DSC curves (Fig. 1b) in the form of two overlapping exothermal effects. At the temperature below 1,000 °C the crystallization of phosphate of the $Ca_9MgK(PO_4)_7$ type takes place and at the temperature above 1,000 °C there follows the formation of magnesium silicate of the Mg_2SiO_4 composition. 4Fe6P glass crystallizes in two, well-separated stages. From XRD examinations it follows that as a result of the first stage of crystallization at 820 °C,

Table 3 Thermal characteristics of crystallization of Fe-doped glasses

Glass	T_c/°C	ΔH_c/J g^{-1}	$\Delta T = T_c - T_g$/°C	Crystallizing phase
02Fe2P	891	200.2	216	$CaMgSiO_4$, $Ca_2MgSi_2O_7$, Mg_2SiO_4
2Fe2P	925	162.3	256	$Ca(Mg_{0.93}Fe_{0.07})SiO_4$
4Fe2P	878	270.8	221	$Ca_{1.003}[Mg_{0.895}Fe_{0.105}]((Si_{1.901}Fe_{0.1})O_6)$, Mg_2SiO_4
02Fe6P	946	195.2	270	$Ca_9MgK(PO_4)_7$, Mg_2SiO_4
2Fe6P	929	230.5	267	$Ca_9MgK(PO_4)_7$, Mg_2SiO_4
4Fe6P	801[a]	67.1	153	$Ca_{19}Mg_{1.56}Fe_{0.44}[PO_4]_{14}$, Mg_2SiO_4

[a] Temperature of the first crystallization peak

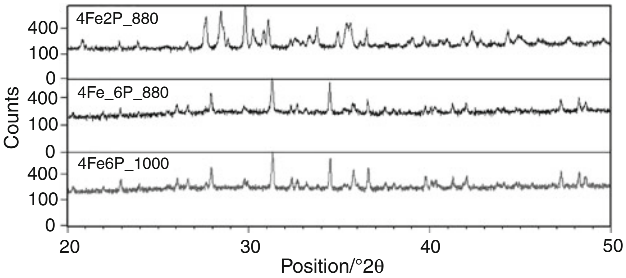

Fig. 3 XRD analyses of selected devitrificates of silicate–phosphate glasses

calcium–magnesium–iron phosphate of the $Ca_{19}Mg_{1.56}Fe_{0.44}[PO_4]_{14}$ composition is formed, and at 989 °C the crystallization of forsterite takes place (Fig. 3).

From the obtained results it follows that the ability for crystallization, its course and the type of the forming phases, in case of silicate–phosphate glass modified by iron additions depend on the relative proportions between iron and phosphorus as components forming the silicate–phosphate structure. The increasing iron amount, in the low phosphorus content glass decreases initially its ability to crystallization, with changing its course and final crystallization only one product, which is the silicate of $Ca(Mg_{0.93}Fe_{0.07})SiO_4$ composition. On the other hand introduction of greater iron amount (4 mol%) makes the crystallization of the amorphous silicate matrix more easy, increasing at the same time the glass tendency to crystallize to final products, which are silicates of ferridiopside ($Ca_{1.003}[Mg_{0.895}Fe_{0.105}]((Si_{1.901}Fe_{0.1})O_6)$) and forsterite ($Mg_2SiO_4$) types.

Simultaneously, the increasing iron amount in the high phosphorus content silicate–phosphate glass makes the crystallization of the amorphous silicate matrix more difficult, increasing at the same time, the glass tendency to crystallize of complex composition phosphates, included in their structure iron ions.

The type of the crystal phases forming in the course of heating the considered glass has been found to be in agreement with the character of the domains occurring in this glass, confirmed by FTIR examinations. Complex and broad character of absorption spectra of the investigated glasses causes that more structural information can be obtained only after their decomposition into separate bands. The spectra of selected glasses after decomposition are presented in Fig. 4.

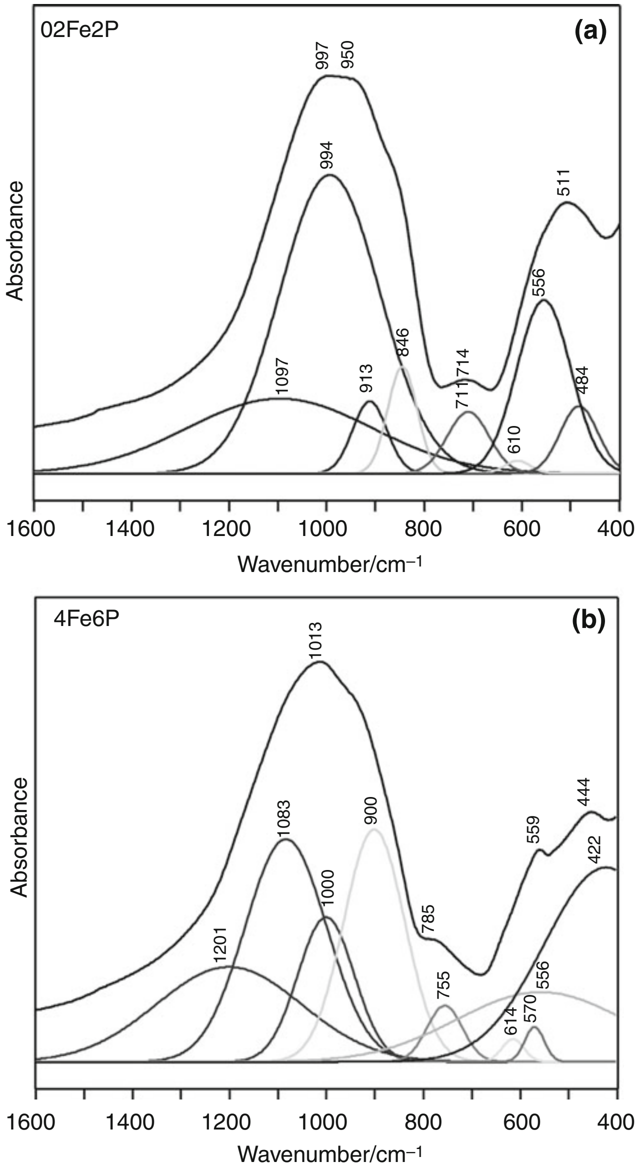

Fig. 4 The decomposition of FTIR spectra of glasses: **a** no 02Fe2P and **b** no 4Fe6P

Decomposition of the absorption bands occurring in the spectrum of the glass containing 2 mol% P_2O_5 and 0.2 mol% Fe_2O_3 indicates the existence of seven component bands at 1097, 994, 913, 846, 610, 556 and 484 cm^{-1}. They correspond to Si–O bonds characteristic for monticellite and forsterite [10] or akermanite [11]. The presence the silicates of these types has been confirmed in the devitrificate by XRD method.

Analysis of the component absorption bands obtained as a result of the decomposition of the spectrum corresponding to the glass containing 6 mol% P_2O_5 and 4 mol% Fe_2O_3 in its structure shows the occurrence of nine bands located at 1201, 1083, 1000, 900, 755, 614, 570, 556 and 422 cm^{-1}. Their positions correspond to the PO_4 vibrations (1083, 1000, 900, 755, 570, 556 cm^{-1}) occurring in phosphate of collinsite type ($Ca_2(MgFe)(PO_4)_2$) [11] and to the SiO_4 vibrations (1000, 900, 614, 422 cm^{-1}) characteristic for forsterite [10].

The FTIR results obtained indicate that the increasing amount of Fe_2O_3 and P_2O_5 in the structure of silicate–phosphate glasses causes formation of domains, whose structure changes from that corresponding to silicates to the one characteristic for phosphates.

Conclusions

Based on DSC, XRD and FTIR studies the influence of iron on the thermal behaviour of SiO_2–P_2O_5–K_2O–CaO–MgO glasses was evaluated. The replacement of MgO and CaO modifiers by Fe_2O_3 results in a decrease of the glass transition temperature T_g and ΔC_p accompanying the glass transition, which show on the appearance of structure strains facilitating the breaking of chemical bonds in the glassy network. On the other hand the ability for crystallization, its course and the type of the forming phases depend on the proportions between iron and phosphorus as components forming the silicate–phosphate structure, and are in agreement with the character of the domains which are formed in the considered glass.

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