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Influence of B_2O_3 on the structure and crystallization of soil active glasses

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Abstract Glasses of the SiO_2–P_2O_5–K_2O–MgO–CaO–B_2O_3 system acting as nutrients carriers in the soil environment were synthesised by the melt-quenching technique. Thermal properties were studied using DTA/DSC methods and the influence of B_2O_3 and P_2O_5 content on thermal stability and crystallization process of these glasses was examined. The structure of the glass network was characterized by FTIR, ^{31}P, and ^{11}B MAS NMR. The chemical activity of the glasses in the 2 mass% citric acid solution was measured by the ICP-AES method. The analysis indicated that the formation of P–O–B units with chemically stable tetrahedral borate groups decreases the glass solubility in conditions simulating the soil environment.

Keywords Crystallization · Dissolution · Glass structure · Silicate–borophosphate glasses

Introduction

It is commonly believed that B_2O_3 is one of the most important glass components showing strong glass forming properties. Often it is introduced into the chemical composition of silicate glasses in order to lower the temperature of their melting and improve their properties, especially their chemical durability and resistance to thermal shocks. Boron improves mechanical properties of glasses as well, strongly affecting the quality of the elasticity module. Moreover, it significantly increases their hardness. These glasses find important large-scale industrial applications as chemically and mechanically resistant materials. B_2O_3 is especially used in technical borosilicate glasses of Pyrex, Simax, or Termisil type, which are widely used as laboratory glasses (Pyrex, Simax) or heat-resisting ones (Termisil), characterized by the high resistance to thermal shocks [1].

Borosilicate glasses with addition of phosphorus are mainly used in fiber optics technology and lasers [2, 3] and in microelectronics as insulating interconnections in integrated circuits [4, 5]. In silicate and borosilicate glasses, P_2O_5 affects the viscosity and melting temperature [6]. The chemical durability of borosilicate glasses usually decreases with phosphate additions, although the durability may increase with the formation of durable crystalline phases on the surface [7, 8]. On the other hand, the dissolution rate of multicomponent borosilicate glasses from the Al_2O_3–B_2O_3–(BaO)–CaO–Fe_2O_3–K_2O–MgO–Na_2O–(PbO)–(P_2O_5)–SiO_2 system increases with increasing B_2O_3 content [9].

It is known that the structure of alkaline borosilicate glasses comprises tetrahedral $[BO_4]^{5-}$, $[SiO_4]^{4-}$ groups and triangular $[BO_3]^{3-}$ groups [10, 11]. Structural examinations of glasses of the K_2O–B_2O_3–SiO_2–P_2O_5 system [12] show that phosphorus in their structure can be found in the form of mono and diphosphate complexes, which form, among others, a connection of the P–O–B type. As a result of the phosphorus incorporation, an increase of both the $[BO_3]/[BO_4]$ ratio and the degree of polymerization of silicate network is observed. Simultaneously, it was found in [13] that the addition of P_2O_5 into the structure of

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borosilicate glasses causes a formation of isolated PO_4^{3-} and $P_2O_7^{4-}$ anions, and $P_2O_7^{4-}$ anions connected to tri-coordinated and tetra-coordinated borate groups. The relative amount of phosphate anions connected to borate groups is related to the optical basicity of borosilicate glasses.

The progress in the glass studies is manifested in the development of new glasses with unconventional properties. There belong, among others, glasses containing in their composition biogenic elements (macroelements—P, Ca, Mg, K, and microelements—B, Cu, Fe, Zn), which release in the form that is available for plants in the soil biological environment. 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%) [14]) can be used in practice as ecological fertilizers providing a controlled release rate of the nutrients for plants [15]. In these glasses, boron plays an important role as a microelement, whose influence on the plants development is related to the nucleic acids synthesis (DNA and RNA) as well as phytohormones. It also controls the flow of saccharides through the cell membranes and effects the development of tissues and organs. Moreover, it takes part in the carbohydrates metabolism. The 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 [16].

The aim of the present work was to determine the relation between the thermal stability and structure of silicate-phosphate glasses modified by the boron addition, as well as their chemical activity under conditions simulating the biological soil environment.

Experimental

Two groups of silicate–phosphate glasses from the SiO_2–P_2O_5–K_2O–CaO–MgO–B_2O_3 system differing in the content of P_2O_5 and containing in its composition an increasing amount of B_2O_3 were prepared. In both groups constant quantities of K_2O and SiO_2 were kept, and the increasing amount of B_2O_3 was introduced at the cost of the decreasing amount of MgO and CaO, with the constant MgO/CaO ratio. The chemical composition of examined glasses is presented in Table 1.

The silicate–phosphate glasses were produced by melting the raw materials mixture, i.e., SiO_2, H_3PO_4, K_2CO_3, MgO, $CaCO_3$, and B_2O_3 at the temperature of about 1450 °C. Then the batch-free glasses were fritted in water.

The thermal stability of obtained glasses was determined by the DTA/DSC measurements conducted on the Perkin-Elmer DTA-7 System, operating in the heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate of 10 °C min^{-1} in a dry nitrogen atmosphere to 1100 °C. The glass transition temperature T_g was determined from the inflection point on the enthalpy curve and the enthalpy of the glass crystallization ΔH_{cryst} was calculated using the 7 Series Perkin-Elmer Thermal Analysis Software Library. The ability of glasses to crystallize was evaluated from the values of crystallization temperature T_{cryst}, the enthalpy of crystallization ΔH_{cryst} and the thermal stability parameter of glasses $\Delta T = T_{cryst} - T_g$. The X-ray diffraction method (X'Pert PRO Diffractometer) was applied to identify the crystalline phases created in the isothermal process of glass heating, in temperatures inferred from the DTA/DSC measurements,.

Table 1 Chemical composition of silicate–phosphate glasses

Name of glass	Contents of components/mol%					
	SiO_2	P_2O_5	K_2O	MgO	CaO	B_2O_3
2P	43.0	2.0	6.0	29.0	20.0	–
04B2P	43.0	2.0	6.0	28.6	20.0	0.4
4B2P	43.0	2.0	6.0	26.5	18.5	4.0
9B2P	43.0	2.0	6.0	23.5	16.5	9.0
6P	41.0	6.0	6.0	28.0	19.0	–
04B6P	41.0	6.0	6.0	27.6	19.0	0.4
4B6P	41.0	6.0	6.0	25.5	17.5	4.0
9B6P	41.0	6.0	6.0	22.5	15.5	9.0

The Fourier transform infrared spectroscopy (FTIR) studies of glasses and their crystallized forms were carried out on the Digilab FTS 60v spectrometers in MIR range (400–4000 cm^{-1}). Samples were prepared in the form of KBr pellets.

Solid state Magic-Angle-Spinning Nuclear Magnetic Resonance (MAS NMR) spectra were measured on the APOLLO console (Tecmag) at the magnetic field of 7.05 T produced by the 300 MHz/89 mm superconducting magnet (Magnex). A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and KEL-F cap was used to spin the sample at 8 kHz.

The ^{31}P MAS NMR spectra were measured at 121.264 MHz, using a single 3 µs rf pulse, corresponding to $\pi/2$ flipping angle. The acquisition delay used in accumulation was 30 s, and 128 scans were acquired. The frequency scale in ppm was referenced to the ^{31}P resonance of H_3PO_4.

The ^{11}B MAS NMR spectra were measured at 96.119 MHz, using a single 2 µs rf pulse, corresponding to $\pi/4$ flipping angle in the liquid sample. The acquisition delay used in accumulation was 1 s, and 128 scans were acquired. The frequency scale in ppm was referenced to the ^{11}B resonance of 1 M solution of H_3BO_3.

The chemical activity of glasses refined to the grain size 0.1–0.3 mm was determined using the test that is generally used in the agricultural chemistry, which is based on their dissolution in 2 wt% citric acid solution. The glass to solution weight ratio was 1:100 [17].

Results and discussion

Thermal studies (DTA/DSC)

The thermal studies show that during the heating process the glasses of the SiO_2–P_2O_5–CaO–MgO–K_2O–B_2O_3 system undergo typical phase changes, namely glass transformation and crystallization effects (Fig. 1).

The effect of chemical composition of the examined glasses on the parameters characterizing these phase transformations are summarized in Table 2.

The introduction of boron and a gradual increase of its amount at the cost of decreasing content of calcium and magnesium, results in a gradual decrease of the glass temperature (T_g).

According to literature, opposite effects, that is an increase of T_g were observed in borophosphate glasses, in which the boron content was increased at the cost of sodium and phosphorus [18], as well as with the constant phosphorus content [19], and in borosilicate glasses, in which the boron content was increased at the cost of sodium, with constant phosphorus and increasing silicon amounts [13].

The DTA/DSC studies further showed a significant decrease of the thermal stability of the low phosphate content glasses (2 mol% of P_2O_5) with the introduction of small boron amount, as manifested by smaller thermal stability parameter ΔT (Table 2). An opposite tendency was found in the high phosphate content glasses (6 mol% P_2O_5), at the same boron amount. Simultaneously, both crystallization temperatures T_{cryst}, and the corresponding crystallization enthalpies ΔH_{cryst} decrease in both groups of glasses with the increase of boron content, reflecting their

Fig. 1 DTA/DSC curves of analysed silicate–phosphate glasses

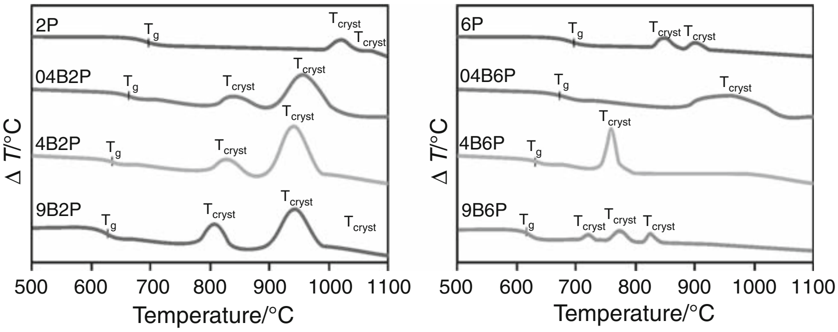

Table 2 Thermal characteristics of silicate–phosphate glasses modified by the addition of B_2O_3 as microelement

Name of glass	T_g/°C	$\Delta T = T_{cryst} - T_g$/°C	T_{cryst}/°C	ΔH_{cryst}/J/g	T_{cryst}/°C	ΔH_{cryst}/J/g	T_{cryst}/°C	ΔH_{cryst}/J/g	Crystalline phase
2P	680	345	1025	67.3	1086	3.7			1025 °C—$CaMgSi_2O_6$ 1086 °C—$CaMgSi_2O_6$
04B2P	667	170	837	24.5	965	104.6			837 °C—$CaMgSi_2O_6$ 965 °C—$CaMgSi_2O_6$
4B2P	642	176	818	26.3	941	141.5			818 °C—$CaMgSi_2O_6$ 941 °C—$CaMgSi_2O_6$
9B2P	635	166	801	43.3	942	100.8			801 °C—$CaMgSi_2O_6$ 942 °C—$CaMgSi_2O_6$
6P	679	165	844	21.7	896	13.9			844 °C—$Ca_9MgK(PO_4)_7$ 896 °C—$Ca_9MgK(PO_4)_7$
04B6P	671	253	924	73.0					$Ca_9MgK(PO_4)_7$
4B6P	645	113	758	49.4					$Ca_{9.93}(P_{5.84}B_{0.16}O_{24})(B_{0.67}O_{1.79})$
9B6P	616	94	710	12.7	782	16.0	834	14.4	710 °C—$Ca_{9.93}(P_{5.84}B_{0.16}O_{24})(B_{0.67}O_{1.79})$ 770 °C—$Ca_9MgK(PO_4)_7$ 834 °C—$Ca_9MgK(PO_4)_7$

increasing ability to crystallization. Additionally, a greater tendency toward crystallization can be noticed in the high phosphate content glasses.

Boron introduction into the low phosphorus content glasses' structure (2 mol% of P_2O_5) does not change the course of their crystallization. It always shows a two step character and is accompanied by significant heat of crystallization ΔH_{cryst} (Table 2). The X-ray diffraction analysis showed that, in spite of the increasing amount of boron in their composition, the crystallization product of these glasses is calcium–magnesium silicate of the diopside type.

In the case of glasses containing 6 mol% P_2O_5 the crystallization process varies, depending on the boron content (Fig. 1). For the 6P glass, which does not contain boron in its composition, crystallization occurs in two steps characterized by small ΔH_{cryst} (Table 2). In both temperatures, the crystallization product is a phosphate of the $Ca_9MgK(PO_4)_7$ type. For 04B6P glass, a single-step crystallization occurs at higher temperature, in a broad temperature range. A complex phosphate of the $Ca_9MgK(PO_4)_7$ composition is identified by XRD as the crystallization product. The 4B6P glass is also characterized by a single crystallization step, but it takes place at a significantly lower temperature, in a narrow temperature range, and is well marked. The calcium phosphate borate of $Ca_{9.93}(P_{5.84}B_{0.16}O_{24})(B_{0.67}O_{1.79})$ composition turned out to be the crystallization product of this glass. The glass containing 9 mol% of B_2O_3 crystallizes in three steps, all characterized by small ΔH_{cryst}. The XRD analysis of the devitrificate annealed at 710 °C found the presence of calcium phosphate borate, while at the temperatures of 782 and 834 °C the phosphate of $Ca_9MgK(PO_4)_7$ composition was identified (Fig. 1).

The types of crystalline phases that were formed in the course of silicate–phosphate glasses heating and were identified by the X-ray diffraction studies, agree well with the results of the Fourier Transform Infrared Spectroscopy (FTIR) studies of these devitrificates (Fig. 2).

In the absorption spectra of the 4B2P_818 °C recrystallized glass, the bands located at about 1071, 969, 870, 676, and 511 cm^{-1} illustrate the presence of vibrational modes of Si–O bonds in the $CaMgSi_2O_6$ silicate [20]. Simultaneously, a band that is visible at 1406 cm^{-1} shows the presence of the B–O stretching mode of BO_3 units. Additional bands are observed in the 1030–450 cm^{-1} range in the case of the glass devitrificate containing a larger amount of phosphorus (4B6P). They are characteristic of bonds occurring in calcium-borates. [21].

The described above changes of parameters characterizing the thermal behavior of silicate–phosphate glasses modified with the addition of boron show that the ability for crystallization, its course and the type of the forming phases depend on relative proportions between the B_2O_3 and P_2O_5 units forming the glass structure. The introduction of boron into the low phosphorus content glass (2 mol% of P_2O_5) increases its ability to crystallize, without changing its course or the final crystallization product, which is the silicate of diopside structure. On the other hand, the boron presence in the high phosphorus content (6 mol% of P_2O_5) silicate–phosphate glasses' structure makes the crystallization of the amorphous silicate matrix more difficult, increasing, at the same time, the glass tendency to crystallize to final products, which are borates and phosphates of complex composition.

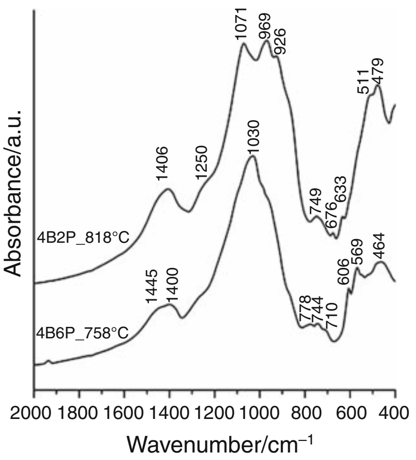

Fig. 2 FTIR spectra of 4B2P and 4B6P recrystallized glasses

Spectroscopic study

FTIR

FTIR spectra in the middle infrared range (MIR) of silicate–phosphate glasses modified by B_2O_3 are presented in Fig. 3. Their interpretation is summarized in Table 3.

The FTIR study shows that the boron introduction into the structure of glasses from the SiO_2–P_2O_5–K_2O–CaO–MgO system containing both small and large phosphorus amounts causes the appearance of absorption bands at about 1420 cm^{-1}, originating from the stretching modes of the B–O bonds of BO_3 units. Simultaneously, a shift of all bands positions toward lower wave numbers shows a depolimerization effect of boron on the silicate–phosphate framework. The primary glass structure, weakened in this way, exhibits lower T_g values, as well as smaller thermal stability (a larger crystallization ability), which was already found with the use of the DTA/DSC method. It was also found that along with the boron increase in glasses containing 6 mol% P_2O_5, a clear separation of absorption bands occurs. They are assigned to symmetric vibrations of the P–O–B oxygen bridges and to bending vibrations of the B–O–B bonds of different units, correspondingly (Table 3).

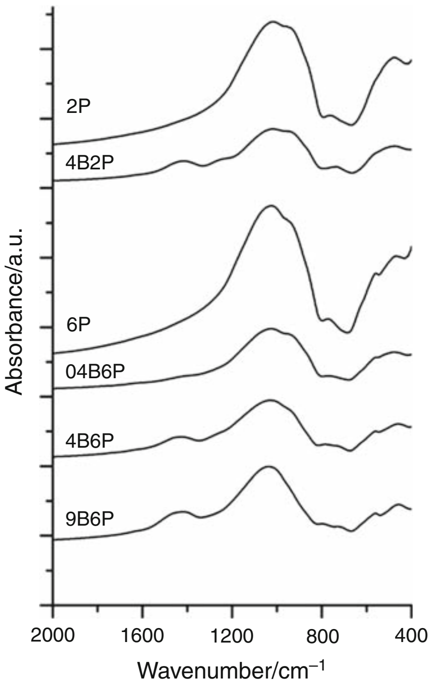

Fig. 3 FTIR spectra of silicate–phosphate glasses

Furthermore, the intensity of the absorption band at about 1030 cm^{-1} increases along with the boron content in the considered glasses group (Fig. 3). The band originates from the B–O stretching mode of BO_4 units. The observations suggest that some changes around the P–O–B bonds in the structure of considered glasses take place. It remains in agreement with the identified earlier compound that is formed during crystallization of this group of glasses, which is a complex calcium phosphate borate.

^{31}P and ^{11}B MAS NMR

^{31}P MAS NMR spectra of two groups of glasses of the SiO_2–P_2O_5–K_2O–CaO–MgO–B_2O_3 system differing in phosphorus content are presented in the Fig. 4a, b, and the spectral parameters obtained from the deconvolution procedure are summarized in Table 4 (FWHH stays for Full Width at Half Height). The ^{31}P spectra of samples that do not contain boron in their composition, i.e., 2P, 6P

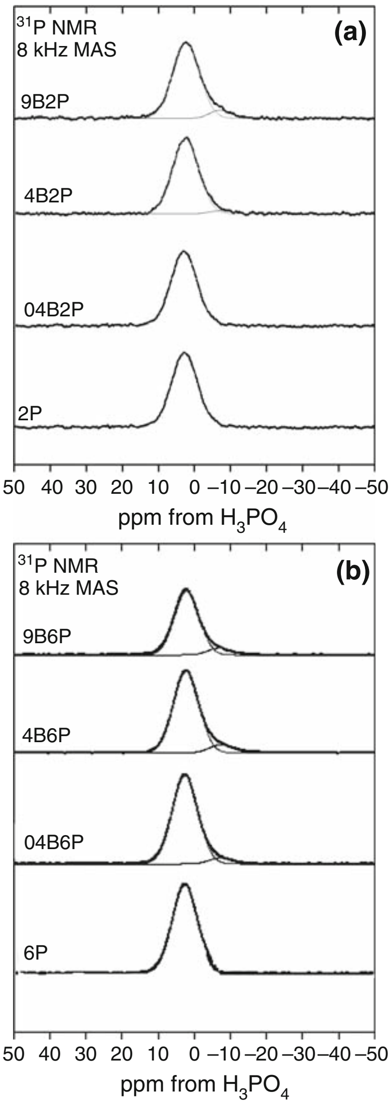

Fig. 4 ^{31}P MAS NMR spectra of silicate–phosphate glasses, after deconvolution procedure

Table 3 Data on absorption bands of SiO_2–P_2O_5–K_2O–CaO–MgO–B_2O_3 glasses

Name of glass	Peak position/cm^{-1}						
	B–O in B_2O_3 [22]	Si–O–Si B–O in BO_4 [22]	P–O–P [23]	P–O–B B–O–B		Si–O–Si O–Si–O	P–O–P Si–O–Si
2P	–	1034	961	776		–	490
4B2P	1420	1020	940	736		–	477
6P	–	1039	956	777		567	478
04B6P	1424	1028	940	770		560	459
4B6P	1429	1030	940	785 725	725	560	459
9B6P	1430	1037	–	798 725	725	560	458

Table 4 ^{31}P and ^{11}B MAS NMR parameters of silicate–phosphate glasses

	^{31}P MAS NMR			^{11}B MAS NMR			
	Chemical shift/ppm	FWHH/ppm	Intensity/%	Type of borate groups	Chemical shift/ppm	FWHH/ppm	Intensity/%
2P	+2.8	7.2	100	–	–	–	–
04B2P	+3.1	8.6	100	Tetra-coordinate	–	–	–
				Tri-coordinate			
4B2P	+2.6	8.6	97	Tetra-coordinate	−19.9	3.6	9
	−7.0	6.8	3	Tri-coordinate			91
8B2P	+2.3	8.8	92	Tetra-coordinate	−19.9	3.9	33
	−7.0	6.7	8	Tri-coordinate			77
6P	+2.2	7.1	100	–	–	–	–
04B6P	+2.6	8.3	95	Tetra-coordinate	−20.0	3.6	17
	−7.0	7.1	5	Tri-coordinate			83
4B6P	+2.3	8.2	91	Tetra-coordinate	−20.3	3.7	23
	−7.3	7.6	9	Tri-coordinate			77
4B6P_758 °C	+3.2	3.9	100	Tetra-coordinate	−20.5	4.4	30
				Tri-coordinate			70
9B6P	+2.1	7.9	91	Tetra-coordinate	−20.5	3.7	45
	−6.9	7.4	9	Tri-coordinate			55

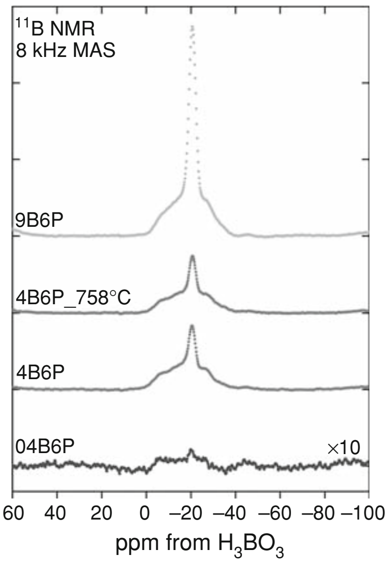

Fig. 5 ^{11}B MAS NMR spectra of silicate–phosphate glasses and devitrificate of 4B6P glass

glasses, exhibit a single, symmetric Gaussian peak characterized by the chemical shift of +2.8 and +2.2 ppm, representing, double phosphate $(P_2O_7)^{4-}$ units [13]. The introduction of small boron amount into the structure of the glasses shifts the peak slightly downfield and increases its width, which means that the polymerization of the phosphate network decreases. Simultaneously, an additional peak appears at −7.0 ppm, which can be assigned to phosphates bonded to borate units [13]. The relative intensity of this peak increases with the boron content, which is more visible in the case of high phosphorus content group of glasses (Table 4). This effect confirms the tendency of phosphorus to form the P–O–B species.

The ^{11}B MAS NMR spectra of studied glasses after decomposition (Fig. 5) show two overlapping resonances attributed to tetra- (about −20 ppm) and tri-coordinated boron atoms [24]. The relative intensity of the peak assigned to the tetra-coordinated boron atoms $[BO_4]$ increases with the boron content (Table 4). Again, this effect is more visible in glasses with the larger phosphorus content.

According to both ^{31}P and ^{11}B MAS NMR studies, the formation of P–O–B units is the result of binding of diphosphate groups with borate groups containing both tri- and tetra-coordinated boron atoms. In addition, the amount of P–O–B (BO_4) units increases with the boron and phosphorus content in the glasses.

Chemical activity

The amount of chemical components released from the examined glasses structure in the citric acid solution as determined by the ICP-AES method is shown in (Fig. 6). The introduction of even small quantity of B_2O_3 (0.4 mol%) into the glass structure increases the solubility of macroelements that are contained in them. It is more visible in the case of glasses with lower P_2O_5 content. About 80–95% of the initial macrocomponent content dissolves from the glass containing 2 mol% P_2O_5 and

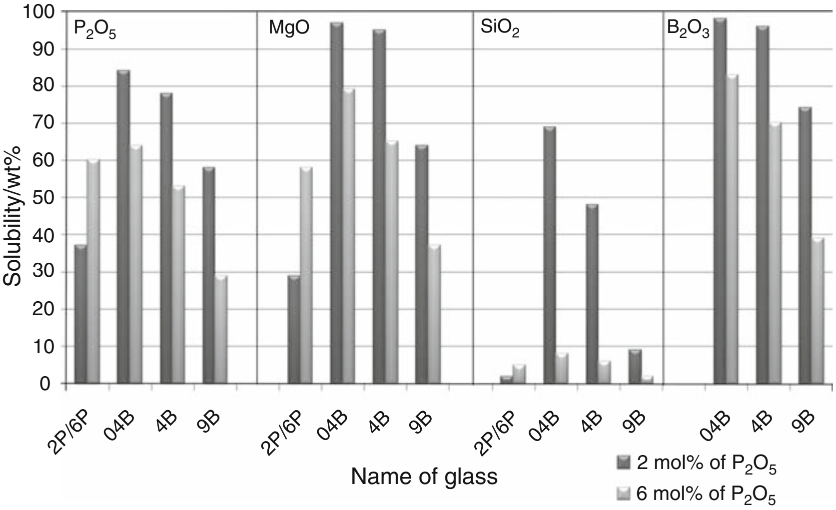

Fig. 6 The solubility of chemical components of silicate–phosphate glasses in 2 mass% citric acid solution

0.4 mol% B_2O_3, while glasses containing 6 mol% of P_2O_5 release only about 65–80%. When the amount of B_2O_3 increases to 4.0 mol%, the release of the glass components decreases to 30–45%. Generally, the solubility of both groups of glasses decreases with increasing content of B_2O_3.

Moreover, the solubility studies indicate that the amount of glass former oxide in the form of P_2O_5 that is introduced into the structure of examined glasses affects the succession of components released during the dissolving process. For glasses containing 2 mol% of P_2O_5, the leaching succession of particular components shown in the form of oxides is following: $B_2O_3 > P_2O_5 > K_2O > CaO > MgO > SiO_2$, whereas in the case of glasses containing 6 mol% of P_2O_5, potassium, calcium, and magnesium are leached quickly, next boron, while phosphorus and silicon show lower rate of dissolution ($K_2O > CaO > MgO > B_2O_3 > P_2O_5 > SiO_2$).

According to the structural studies presented earlier, such behavior of the examined glasses is the result of increasing amount of P–O–B (BO_4) units in their structure. Formation of such domains with chemically stable tetrahedral borate groups decreases the chemical activity of considered glasses.

Conclusions

Boron plays an important role as a microelement that is necessary in the growth process of plants. Silicate–phosphate glasses with boron addition find application as slow release fertilizers. On the basis of spectroscopic (FTIR, MAS NMR), X-ray diffraction (XRD) and thermal (DTA/DSC) studies, the influence of boron addition on the structure of silicate–phosphate glasses was evaluated. It was found that the phosphate network in glasses containing modifiers in the form of K, Ca, and Mg consists of $(P_2O_7)^{4-}$ units, whereas the boron introduction causes the P–O–B species formation. They are created as a result of binding of $(P_2O_7)^{4-}$ units with boron groups containing both tri- and tetra-coordinated boron atoms. Along with the boron and phosphorus content increase in the glasses structure, the amount of P–O–B (BO_4) units increases. The presence of P–O–B bonds was confirmed by the formation of calcium-phosphate borate, being the glass crystallization product, which contains in its structure boron in both triangular and tetrahedral coordinations. Simultaneously, the formation of P–O–B units with chemically stable tetrahedral borate groups decreases the glass solubility in conditions simulating the soil environment. This means that the use of glassy fertilizers with smaller phosphorus amount, as boron microelement carriers, is more effective for agriculture.

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