

Effect of glass composition on the interactions between structural elements in Cu-containing silicate–phosphate glasses

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Abstract The structure of silicate–phosphate glasses from the $\text{SiO}_2\text{–P}_2\text{O}_5\text{–K}_2\text{O–CaO–MgO–CuO}$ system acting as slow release fertilizers, containing different amounts of copper ions replacing magnesium or calcium ions, was examined by DSC, XRD, ^{31}P , and ^{29}Si MAS–NMR techniques. The chemical activity of the glasses in the 2 mass% citric acid solution was measured by the ICP–AES method. The studies showed that regardless of the kind of replaced components, the Cu ions prefer to associate with the phosphorous Q^1 units, forming the domains composed of orthophosphate with P–O–Cu bonds. The formation of domains with chemically stable P–O–Cu bonds resulted in poorer glass solubility under conditions simulating the natural soil environment.

Keywords Silicate–phosphate glasses · CuO · Structure · Crystallization · Chemical activity

Introduction

Current views on the glass structure combine the Zachariasen–Warren’s theory of continuous network [1] and the Lebediev’s crystalline theory [2]. It is commonly assumed that regions with high degree of disorder coexist with

partially ordered domains of the size larger than a single tetrahedron, but not exceeding a few hundreds of nanometers. The evidence for the presence of such microregions (domains or clusters) is provided by spectroscopic and diffraction studies. For example, the infrared-absorption spectra of $\nu\text{-SiO}_2$ and high-temperature phase of crystal ballite show a striking similarity [2]. Structural studies of silicate–phosphate glasses indicated that they are also characterized by the domain structure. The domains can differ in chemical compositions [3, 4], and they are also a crystalline nucleus, which determines the phase appearing during thermal heating of the glass. Therefore, the determination of the crystalline analogs of the glass precursors allows to infer the domains structure. The structure of domains effects also the chemical activity of the glass [5, 6].

Multicomponent silicate–phosphate glasses from the $\text{SiO}_2\text{–P}_2\text{O}_5\text{–K}_2\text{O–CaO–MgO–CuO}$ system started recently to be used as ecological fertilizers releasing the macroelements (P, Ca, Mg, K) with the controlled rate [7, 8]. Such glassy fertilizers can also act as carriers of copper, which plays an active role in many life processes of plants, such as photosynthesis, respiration, metabolism of nitrogen compounds, carbohydrate transport, as well as proteins and RNA/DNA formation [9]. An optimum amount of copper is required for the normal development of plants, because its deficiency and excess may have some adverse effects.

Our initial studies of the $\text{SiO}_2\text{–P}_2\text{O}_5\text{–K}_2\text{O–CaO–MgO–CuO}$ glass showed a reduction of their chemical activity with an increase of CuO at the cost of decreasing amount of MgO and CaO with constant MgO/CaO ratio [10]. It was suggested that it is due to formation of domains containing chemical durable P–O–Cu bonds. The aim of the present work was to confirm this hypothesis by comprehensive thermal and spectroscopic studies of the glass domain structure, thermally induced crystallization products, and

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the chemical activity under conditions simulating the biological soil environment. For that purpose, a series of glasses from the $\text{SiO}_2\text{-P}_2\text{O}_5\text{-K}_2\text{O-CaO-MgO-CuO}$ system in which Ca or Mg ions were gradually replaced by Cu ions were investigated by DSC, XRD, and MAS-NMR methods.

Experimental

Two series of silicate-phosphate glasses from the $\text{SiO}_2\text{-P}_2\text{O}_5\text{-K}_2\text{O-CaO-MgO-CuO}$ system differing in the CuO, CaO, and MgO content were prepared. In both groups constant quantities of P_2O_5 , K_2O , and SiO_2 were kept. The increasing amount of CuO replaced either CaO or MgO, keeping the content of the other component constant. The silicate-phosphate glasses were produced by melting the mixture of raw materials, i.e., SiO_2 , H_3PO_4 , MgO, K_2CO_3 , CaCO_3 , and CuO at $1,450\text{ }^\circ\text{C}$. Then the obtained melts were fritted in water. The glasses were ground to the particle size of 0.1–0.3 mm. The nominal chemical composition of synthesized glasses is presented in Table 1. The CaMgCu designation of the glass samples indicates their variable CaO, MgO, and CuO content.

The X-ray diffraction (XRD) method using the X'Pert PRO Diffractometer (Philips) was applied to confirm the amorphous state of the synthesized glasses, with the results shown in the Table 1. Further studies were conducted on the amorphous samples only.

The crystallization of glasses was determined by the differential scanning calorimetry (DSC) measurements conducted on the STA 449 F1 Jupiter (Netzsch) apparatus, operating in the heat flux DSC mode. Five reference substances i.e.: indium, tin, bismuth, aluminium, and gold were used for temperature calibration. The 60 mg samples containing the particles of 0.1–0.3 mm size were heated to $1,100\text{ }^\circ\text{C}$ in the platinum crucibles at the rate of $10\text{ }^\circ\text{C min}^{-1}$ in a dry nitrogen atmosphere. The glass transformation temperature T_g and the crystallization temperature T_c were determined as the midpoint of the change in the specific heat C_p in the glass transformation region, and as the onset of the first crystallization peak, respectively. The Netzsch Proteus Thermal Analysis program (version 5.0.0) was used to evaluate the thermal parameters of the samples. The ability of glasses to crystallize was estimated from the values of the thermal stability parameter of glasses (ΔT) determined as

$$\Delta T = T_{\text{onset1}} - T_g \quad (1)$$

where T_{onset1} is the onset temperature of the first crystallization stage and T_g is the glass transition temperature of the given sample.

In order to identify crystallization products, separate samples were isothermally heated for 5 h at the crystallization temperatures T_c that were inferred from the DSC measurements. The resulted crystalline phases were detected and identified by XRD.

The local glass structure was investigated using ^{29}Si and ^{31}P MAS-NMR spectroscopy. The solid state ^{29}Si and ^{31}P MAS-NMR spectra were measured by the APOLLO console (Tecmag) using the 7 T/89 mm superconducting magnet (Magnex). A Bruker HP-WB high-speed MAS probe equipped with the 4 mm zirconia rotor and the KEL-F cap was used to spin the sample at 4 and 8 kHz, for the ^{29}Si and ^{31}P measurements, respectively. A single 3 μs rf pulse, corresponding to $\pi/2$ flipping angle, was applied. The acquisition delay in accumulation was 30 s, and 128 scans were acquired in the ^{31}P measurements. The number of scans in the ^{29}Si measurements ranged from 256 to 400, and the spectral intensities were normalized accordingly. A 50 Hz Lorentzian line broadening was applied to the spectra, which was equal to about 0.8 and 0.4 ppm for the silicon and phosphorus, correspondingly. The frequency scale in ppm was referenced to TMS and 85 % mol H_3PO_4 for the ^{29}Si and ^{31}P spectra, respectively.

Chemical activity of the glasses was determined using the test that is commonly used in agricultural chemistry. The samples are put into 2 mass% citric acid solution, which simulates the action of organic compounds released by the plant roots to extract the useful components from mineral fertilizers [11]. The mass ratio of the glass to the solution was 1:100. Such proportions of glassy fertilizers to extraction solution simulate conditions of the natural soil environment. The prepared suspensions of the glass particles were stirred for 0.5 h at 350 rpm at $25\text{ }^\circ\text{C}$ and then filtered. The quantitative analysis of the filtrate was carried out using inductively coupled plasma atomic emission spectroscopy ICP-AES method (OPTIMA 7300DV spectrometer). The amounts of selected elements released from the glass particles to the solution were determined.

Results and discussion

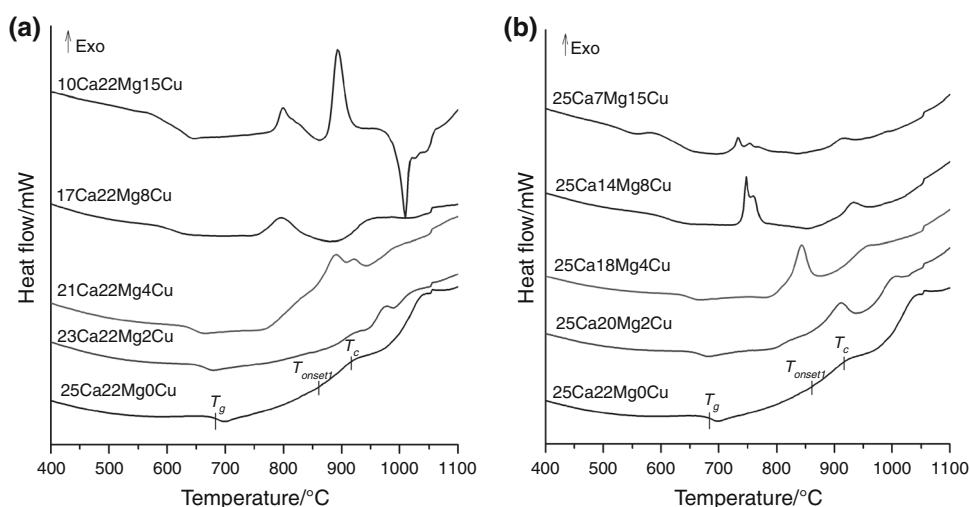
Thermal studies

Characteristic glass transformation and exothermic effects related to glass crystallization were observed on the DSC curves (Fig. 1a, b). The obtained glasses are characterized by multistage crystallization; the number of the exothermic effects depends on their chemical composition, and many of them overlap. The numerical results of the thermal analysis are presented in Table 2.

Some interesting effects are observed in the thermal stability of the glasses as a function of CuO content. An

Table 1 The chemical composition of the silicate–phosphate glasses from the SiO₂–P₂O₅–K₂O–CaO–MgO–CuO system

Glass name	Chemical composition/mol%						State of material
	SiO ₂	P ₂ O ₅	K ₂ O	CaO	MgO	CuO	
25Ca22Mg0Cu	41	6	6	25	22	–	Amorphous
23Ca22Mg2Cu	41	6	6	23	22	2	Amorphous
21Ca22Mg4Cu	41	6	6	21	22	4	Amorphous
17Ca22Mg8Cu	41	6	6	17	22	8	Amorphous
10Ca22Mg15Cu	41	6	6	10	22	15	Amorphous
0Ca22Mg25Cu	41	6	6	–	22	25	Partially crystalline
25Ca20Mg2Cu	41	6	6	25	20	2	Amorphous
25Ca18Mg4Cu	41	6	6	25	18	4	Amorphous
25Ca14Mg8Cu	41	6	6	25	14	8	Amorphous
25Ca7Mg15Cu	41	6	6	25	7	15	Amorphous
25Ca0Mg22Cu	41	6	6	25	–	22	Partially crystalline

Fig. 1 DSC curves of the glasses containing a constant amount of **a** MgO **b** CaO

introduction of small amount of CuO (2 mol%) irrespective of the kind of replaced component (CaO or MgO) increases their thermal stability from 175 °C for copper-free glass to 219 and 187 °C for the 23Ca22Mg2Cu and 25Ca20Mg2Cu glasses, respectively (Table 2). Further substitution of CaO by CuO (up to 8 mol%) first reduces their thermal stability to $\Delta T = 129$ °C for the 17Ca22Mg8Cu glass, and then increases to $\Delta T = 145$ °C for the 10Ca22Mg15Cu glass. On the other hand, the addition of CuO up to 15 mol% in place of MgO gradually decreases the thermal stability to $\Delta T = 94$ °C for the 25Ca7Mg15Cu glass.

XRD reveals that after 5 h of isothermal heating of copper-free sample (25Ca22Mg0Cu) at 925 °C, a mixed calcium–magnesium silicate of diopside-type $\text{CaMgSi}_2\text{O}_6$ and calcium–magnesium–potassium orthophosphate ($\text{Ca}_9\text{MgK}(\text{PO}_4)_7$) phase crystallizes (Table 2).

The crystallization of the 23Ca22Mg2Cu sample is manifested on the DSC curve in the form of three exothermic effects with maxima at 928, 972, and 1,020 °C (Fig. 1a). The heat treatment of this sample at all three crystallization temperatures produced the diopside $\text{CaMgSi}_2\text{O}_6$, $\text{Ca}_9\text{MgK}(\text{PO}_4)_7$, as well calcium–copper orthophosphate $\text{Ca}_{19}\text{Cu}_2(\text{PO}_4)_{14}$ crystals. The same crystallization products were detected in the case of the 25Ca20Mg2Cu glass, which exhibits only two peaks on the DSC curve (Fig. 1b).

Three overlapping exothermic effects are observed on the DSC curve for the 21Ca22Mg4Cu sample. When it is heated at 887 and 921 °C, the same crystallization products as before are identified by XRD, and the diffraction pattern for the latter case is shown on Fig. 2. In contrast, the DSC curve for the 25Ca18Mg4Cu sample shows two well-separated peaks with maxima at 842 and 954 °C. Apart from

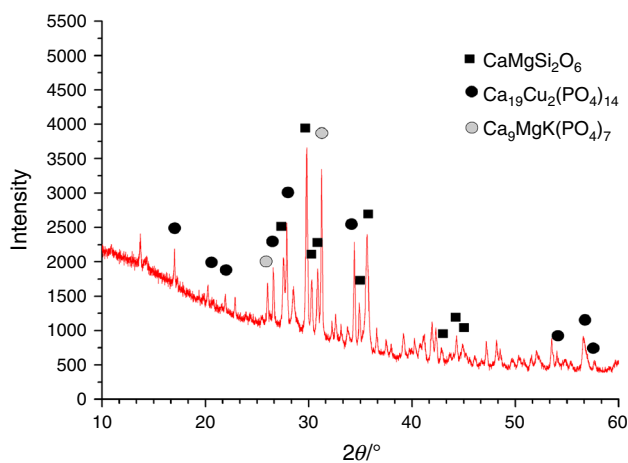
Table 2 Results of thermal and XRD analysis of the silicate–phosphate glasses

Glass name	$T_g/^\circ\text{C}$	$T_{\text{onset1}}/^\circ\text{C}$	$\Delta T/^\circ\text{C}$	$T_c/^\circ\text{C}$	Crystalline phase (ICSD code)
25Ca22Mg0Cu	690(2)	865(2)	175	925(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₂ (08-5109)
23Ca22Mg2Cu	671(2)	890(2)	219	1,036(2) 928(2)	n.a. CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
				972(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
				1,020(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
21Ca22Mg4Cu	643(2)	770(2)	127	887(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
				921(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
17Ca22Mg8Cu	618(2)	747(2)	129	797(2)	Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011) CaMgSi ₂ O ₆ (03-0522)
				948(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
10Ca22Mg15Cu	629(2)	774(2)	145	800(2)	K ₂ Cu ₂ Mg ₃ Si ₁₂ O ₃₀ (02-4259) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011) Ca ₉ MgK(PO ₄) ₇ (08-5109) CuO (08-7122)
				893(2)	K ₂ Cu ₂ Mg ₃ Si ₁₂ O ₃₀ (02-4259) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011) Ca ₉ MgK(PO ₄) ₇ (08-5109) CuO (08-7122)
25Ca20Mg2Cu	668(2)	855(2)	187	911(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
				1,001(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
25Ca18Mg4Cu	653(2)	792(2)	139	842(2)	Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011) Ca ₁₀ (PO ₄) ₆ O (08-7727) CaMgSi ₂ O ₆ (03-0522)
				954(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)

Table 2 continued

Glass name	$T_g/^\circ\text{C}$	$T_{\text{onset1}}/^\circ\text{C}$	$\Delta T/^\circ\text{C}$	$T_c/^\circ\text{C}$	Crystalline phase (ICSD code)
25Ca14Mg8Cu	605(2)	735(2)	130	747(2)	Ca ₁₀ (PO ₄) ₆ O (08-7727) CuO (08-7122)
				932(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
					n.a.
25Ca7Mg15Cu	617(2)	711(2)	94	733(2)	Ca ₁₀ (PO ₄) ₆ O (08-7727) CuO (08-7122)
				754(2)	CaMgSi ₂ O ₆ (03-0522) Ca ₉ MgK(PO ₄) ₇ (08-5109) Ca ₁₉ Cu ₂ (PO ₄) ₁₄ (05-0011)
				912(2)	

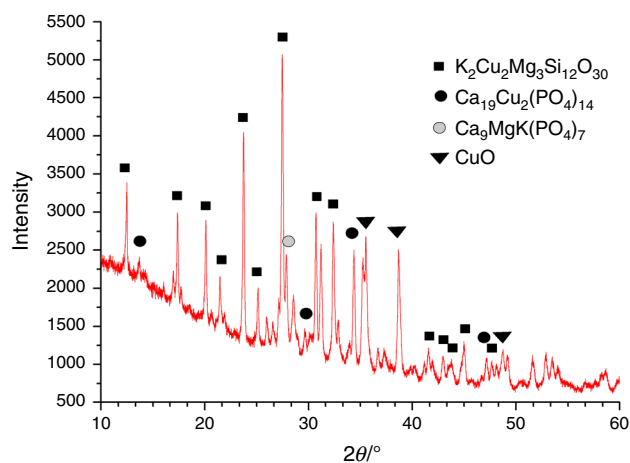
T_g glass transition temperature, T_{onset1} onset temperature of the first crystallization peak, T_c crystallization temperature, *n.a.* not available, in brackets code of crystalline products from the ICSD database

**Fig. 2** XRD pattern of the 21Ca22Mg4Cu glass after heating at 921 °C

the CaMgSi₂O₆, Ca₉MgK(PO₄)₇, and Ca₁₉Cu₂(PO₄)₁₄ crystallization products that were found at both temperatures of heat treatment, an additional oxyapatite Ca₁₀(PO₄)₆O phase was present at lower temperature (843 °C).

The crystallization process of the 17Ca22Mg8Cu glass occurs in two well-separated steps, producing the same crystalline phases as before. On the other hand, the 25Ca14Mg8Cu glass crystallizes in the three steps, two of which partially overlap. While at higher heat treatment temperature three standard crystalline phases are formed, an oxyapatite (Ca₁₀(PO₄)₆O) and CuO were found by XRD at lower temperature (747 °C).

The 10Ca22Mg15Cu glass crystallizes in two overlapping stages in the 774–860 °C range and one well-separated stage with maximum at 893 °C. However, regardless of the heating temperature, XRD reveals the formation of

**Fig. 3** XRD pattern of the 10Ca22Mg15Cu glass after heating at 799 °C

cyclo-silicate of the K₂Cu₂Mg₃Si₁₂O₃₀ composition, the (Ca₉MgK(PO₄)₇ and Ca₁₉Cu₂(PO₄)₁₄) phosphates, as well as CuO (Fig. 3). The 25Ca7Mg15Cu glass exhibits a similar behavior, with slightly different peak heights and positions. The heat treatment at 754 °C produces an additional Ca₁₀(PO₄)₆O phase.

The crystallization processes discussed above produce a mixed calcium–magnesium silicate phase of diopside-type CaMgSi₂O₆, and the mixed calcium–magnesium–potassium orthophosphate (Ca₉MgK(PO₄)₇) in almost all samples studied and at all heat treatment temperatures. Additionally, with an increasing CuO content, a crystalline orthophosphate of the Ca₁₉Cu₂(PO₄)₁₄ composition appears. The same products were found in the case of crystallization of the silicate–phosphate glasses to the structure of which the increasing amount of CuO was

Fig. 4 ^{31}P MAS–NMR spectra of glasses containing a constant amount of **a** MgO **b** CaO. The insets show the full spectral range with spinning sidebands marked by asterisks

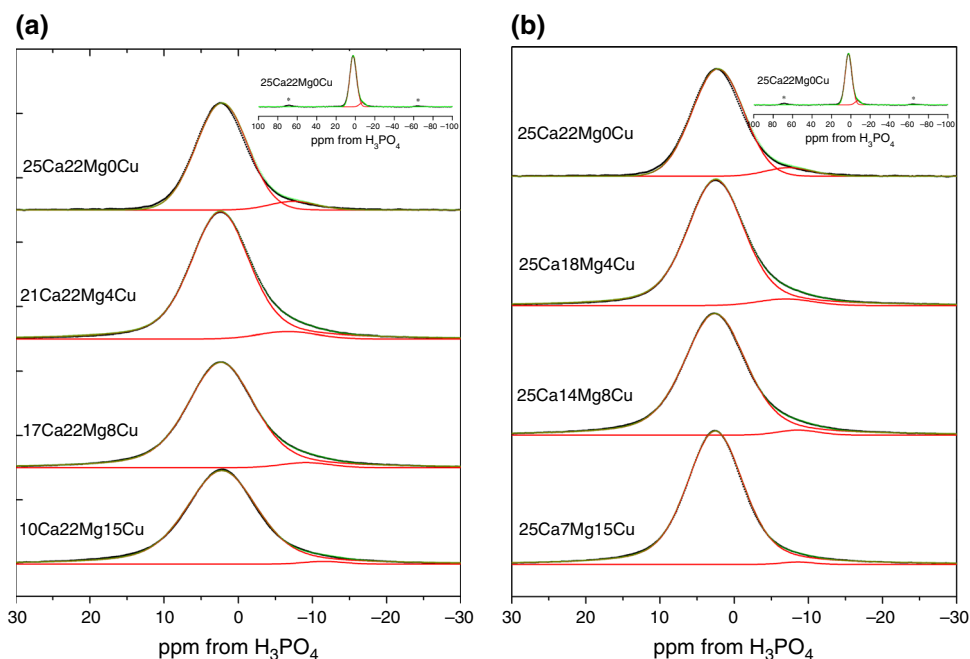
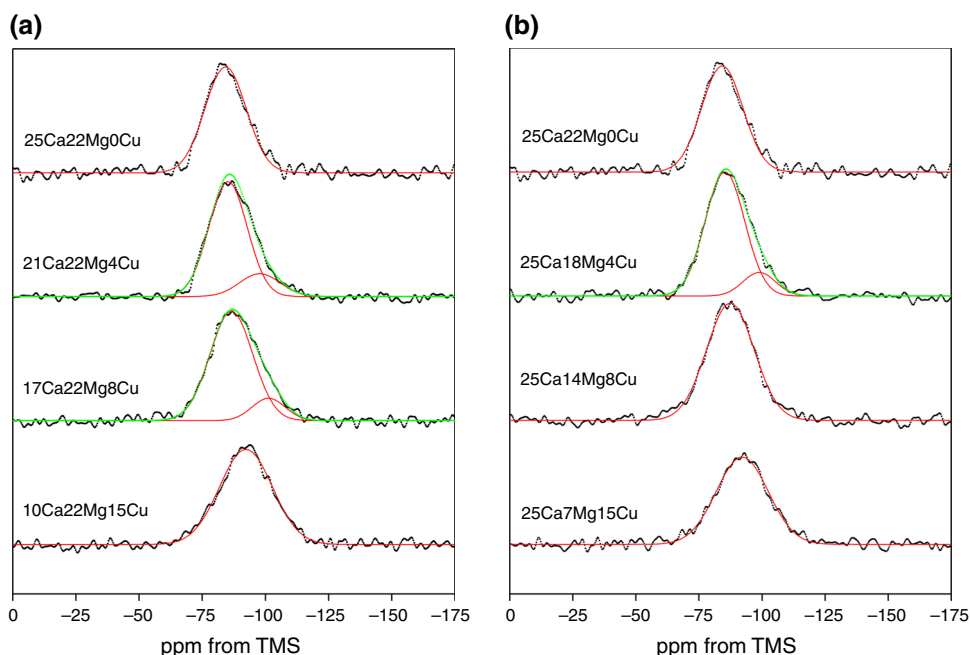


Fig. 5 ^{29}Si MAS–NMR spectra of glasses containing a constant amount of **a** MgO **b** CaO



introduced at the cost of decreasing amount of MgO and CaO, with the constant MgO/CaO ratio [12].

When an increasing amount of CuO replaces CaO, the silicates formed during crystallization change gradually from a chain silicate structure typical for the diopside, to a structure corresponding to ring silicates containing copper of the $\text{K}_2\text{Cu}_2\text{Mg}_3\text{Si}_{12}\text{O}_{30}$ composition. On the other hand, when an increasing amount of CuO replaces MgO, only chain silicates of the diopside composition are produced during crystallization.

MAS–NMR studies

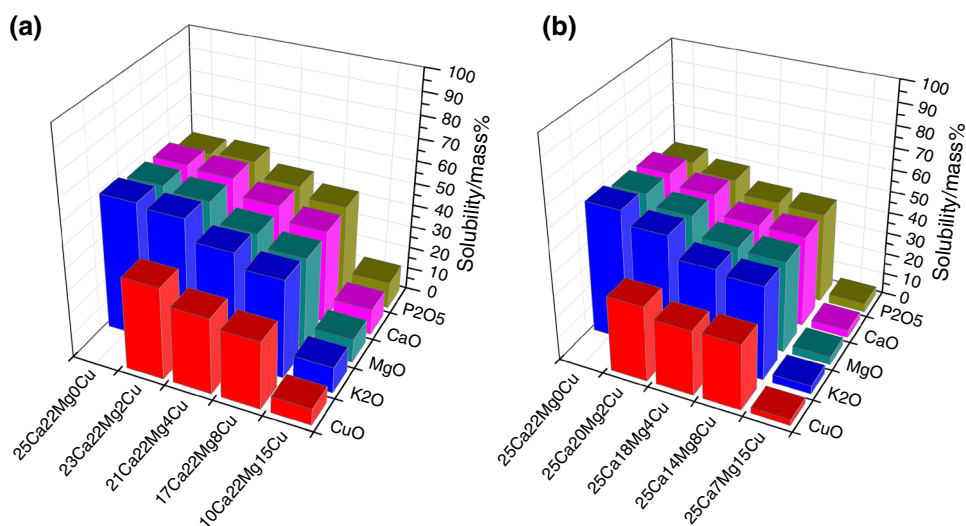
The solid state ^{31}P and ^{29}Si MAS–NMR spectra of glasses from the $\text{SiO}_2\text{--P}_2\text{O}_5\text{--K}_2\text{O--CaO--MgO--CuO}$ system are presented in Fig. 4 and 5, respectively. The parameters of observed peaks, i.e., their positions and widths that were obtained from the deconvolution procedures (Gauss or Lorentz) are listed in Table 3. The uncertainty of the peaks positions is about ± 0.1 ppm.

Table 3 ^{31}P and ^{29}Si MAS–NMR spectral parameters of the silicate–phosphate glasses

Glass name	^{31}P MAS–NMR			^{29}Si MAS–NMR		
	Chemical shift/ppm	FWHM/ppm	Relative contribution/%	Chemical shift/ppm	FWHM/ppm	Relative contribution/%
25Ca22Mg0Cu	+2.3	8.2	93	−84.3	18.6	100
	−7.3	7.5	7			
21Ca22Mg4Cu	+2.5	9.4	96	−84.8	17.9	83
	−6.6	9.1	4			
17Ca22Mg8Cu	+2.5	10.7	97	−86.2	20.1	91
	−9.0	7.8	3			
10Ca22Mg15Cu	+2.1	11.3	99	−91.9	24.6	100
	−11.4	6.5	1			
25Ca18Mg4Cu	+2.6	9.1	96	−85.0	18.4	86
	−6.8	8.7	4			
25Ca14Mg8Cu	+2.7	10.0	98	−87.1	22.3	100
	−8.5	6.6	2			
25Ca7Mg15Cu	+2.7	9.0	99	−91.8	24.3	100
	−8.4	4.9	1			

FWHM full width at half maximum

Fig. 6 Chemical activity of the silicate–phosphate glasses components in 2 mass% citric acid solutions: series containing a constant amount of **a** MgO **b** CaO



The dominant peaks in the ^{31}P MAS–NMR spectra of all glasses studied are located in the +2.1 to +2.7 ppm range (Fig. 4). They represent the orthophosphate units Q° (PO_4^{3-}) in their structure [13, 14]. Small, but statistically significant contributions from pyrophosphate units Q^1 ($\text{P}_2\text{O}_7^{4-}$) are also observed, which are located in the −11.4 to −6.6 ppm range [14]. In both groups of glasses, when the amount of CuO increases, the relative contribution of the pyrophosphate units Q^1 decreases. This effect can be caused by breaking the oxygen P–O–P bridges that are present in the structure of pyrophosphate units (Q^1) and the formation of $\text{P}(\text{PO}_4^{3-})\text{–O–Cu}$ bonds.

This explanation is in good agreement with the results of thermally induced crystallization processes of glasses,

which indicate the presence of complex phosphate of the $\text{Ca}_{19}\text{Cu}_2(\text{PO}_4)_{14}$ type among crystallization products of all glasses studied. This in turn suggests the presence of phospho-oxygen domains in the amorphous matrix, which are composed of orthophosphate units with P–O–Cu bonds, favoring the subsequent crystallization of calcium–copper orthophosphates. Rebuilding the structure of phospho-oxygen domains by introduction of copper may be the reason for change of their thermal stability.

Although the observed large linewidths are typical for a noncrystalline material, their systematic increase with increasing copper content that is apparent in both series of glasses suggests a growing local disorder in the phospho-oxygen units.

^{29}Si MAS–NMR spectra for the all studied glasses (Fig. 5) exhibit a dominant peak located in the -84.3 to -91.9 ppm range, which represents the Q^2 silicate units—containing two bridging oxygen atoms in their structure [15]. A systematic shift of the peak position toward lower frequency (from -84.3 to about -92 ppm) with increasing CuO content suggests the appearance of Q^3 units in the silico-oxygen domains of the glass [15].

When up to 4 mol% of CuO is introduced to the structure of both groups of glasses, a small, but statistically significant peak appears in the ^{29}Si MAS–NMR spectra in the -100.9 to -98.5 ppm range, suggesting the presence of more polymerized silicate units Q^4 , containing four bridging oxygens [16]. It is not present at higher CuO contents. Although the deconvolution of the ^{29}Si MAS–NMR spectra clearly indicates the presence of these rather small contributions, it may seem highly speculative. It is based on the departure of the observed line from a symmetric Gaussian shape that is usually observed in the amorphous materials, and the location is based on the literature data.

Nevertheless, the ^{29}Si MAS–NMR results confirmed the presence of silico-oxygen domains in the examined glasses, composed of silicate Q^2 units of the diopside structure, which was previously identified by the XRD study of their crystalline analogs. Similarly, the indirect detection of the Q^3 units is compatible with the composition of $\text{K}_2\text{Cu}_2\text{Mg}_3\text{Si}_{12}\text{O}_{30}$ compound—the silicate phase precipitating at higher CuO contents, and at higher temperature than the crystallization temperature of diopside. This may be the reason for the observed increase of thermal stability ΔT (Table 2).

A small amount of Q^4 units that is observed in some samples suggests their participation in the structure of diopside [15], or in the dispersed phase of amorphous silica [16].

Chemical activity

Silicate–phosphate glasses offer great possibilities for application as glassy copper carriers as they dissolve in natural soil environment, and their degradation rate can be easily controlled by altering their composition.

The amounts of selected chemical components released from the structure of examined glasses in the 2 mass% citric acid solutions as determined by the ICP–AES method are shown in Fig. 6. The results are presented in mass fraction of a given compound (oxide) that was introduced to the glass batch.

ICP–AES results show a systematic decrease of chemical activity with increased CuO content, regardless of which cations (Ca or Mg) were replaced by the Cu cations. About 50 mass% of the initial components is dissolved from the glasses containing 2 mol% of CuO

(23Ca22Mg2Cu and 25Ca20Mg2Cu samples). When the amount of CuO is increased to 15 mol%, the solubility drops to about 11 and 4 mass%, for the 10Ca22Mg15Cu and 25Ca7Mg15Cu glasses, respectively. According to thermal and structural studies presented earlier, such behavior is caused by the formation of orthophosphate domains of $\text{Ca}_{19}\text{Cu}_2(\text{PO}_4)_{14}$ compositions that contain chemically stable P–O–Cu bonds.

Conclusions

Increasing amount of CuO was incorporated into the structure of glasses from the SiO_2 – P_2O_5 – K_2O – CaO – MgO – CuO system, gradually replacing CaO or MgO. The composition of these glasses was derived from that of the glassy fertilizers developed for agriculture. The effect on the structure and chemical activity of resulted samples was evaluated by spectroscopic and thermal methods. It was found that regardless of which modifier (CaO or MgO) was replaced by CuO, a high-chemical affinity of copper to phosphorous is responsible for the formation of phospho-oxygen domains, which are composed of orthophosphate units with P–O–Cu bonds. The formation of an increasing amount of such chemically stable bonds with increasing CuO content caused a gradual decrease of chemical activity of glasses in the solution simulating the soil environment conditions.

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