



## Structural role of Cu in the soil active glasses<sup>#</sup>

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### Abstract

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 were synthesized by the melt-quenching technique. Influence of copper addition on structure of the glasses was evaluated by XRD, SEM, FT-IR and Raman spectroscopy. Chemical activity of the glasses in 2 wt.% citric acid solutions was measured by ICP-AES method. It has been found that increasing content of phosphorous increased solubility of copper in the structure of the studied glasses which was the result of formation of P-O-Cu bonds.

**Keywords:** glassy fertilizers, structural characterization, FT-IR, Raman spectroscopy, XRD

### I. Introduction

CuO in glasses is mainly used as a pigment. Depending on its concentration and glass composition CuO colors it light blue or blue-green by means of the ionic coloration. On the contrary  $\text{Cu}_2\text{O}$  does not color glasses and thus it is not used as a pigment [1,2]. In the presence of reducing agents  $\text{Cu}_2\text{O}$  is easily reduced to metallic copper which gives a red color to the glass (colloidal coloration) [1,2]. It is worth noting that copper always occurs in glass structure at different oxidation states namely;  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$  and rarely as Cu regardless which copper oxide was introduced to the glass batch. During melting of batch-free glasses in reducing conditions copper dominates in the form of  $\text{Cu}^{2+}$  ions.

Progress in studies of glass is manifested by the development of new glasses with unconventional properties. Among them there are glasses containing biogenic elements like macroelements (P, K, Ca and Mg) and microelements (B, Cu, Fe and Zn) in their composition which are released in biological environment of soil in a form available for plants. Recently, this type of silicate-phosphate glasses started to be used as ecological fertilizers providing a controlled, constant release rate of the nutrients for plants [3,4]. Dissolution rate of particular components of the glasses depend on their chemi-

cal composition and particularly on the content of  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$  which are agents causing depolymerization of the silicate framework of the glass, and it may be controlled in a wide range by appropriate selection of these components. Structure of this type of glasses is capable of receiving atoms of a series of elements acting as microelements, e.g. Fe [5] and B [6].

Copper plays an important role as a microelement and its influence on plants growth process is related to their photosynthesis, respiration, metabolism of nitrogen compounds, formation of proteins, carbohydrate transport and formation of RNA and DNA [7]. The chemical activity of such glasses in the soil environment strongly depends on the type and amount of components and their position in the glass network.

The aim of the present work was to determine the relation between the structure of silicate-phosphate glasses from the  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-K}_2\text{O-MgO-CaO}$  system modified by CuO addition as well as their chemical activity under conditions simulating the biological soil environment.

### II. Experimental

Two groups of silicate-phosphate glasses from the  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-K}_2\text{O-MgO-CaO-CuO}$  system differing in content of  $\text{P}_2\text{O}_5$  and CuO were prepared. In both groups concentrations of  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  were kept constant and the increasing amount of CuO was introduced at the cost of decreasing amount of MgO and CaO with the constant MgO/CaO ratio.

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The silicate-phosphate glasses were produced by melting a mixture of raw materials, i.e.  $\text{SiO}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{MgO}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{CuO}$  at  $1450^\circ\text{C}$ . Then the batch-free glasses were fritted in water. The obtained glasses were grinded and screened to the grain size  $0.1\text{--}0.3\text{ mm}$ .

Chemical composition of the synthesized glasses was determined by the X-ray fluorescence spectrometry (XRF) method, using ARL ADVANT'XP Spectrometer. The X-ray diffraction method (X'Pert PRO Diffractometer) was used to confirm the amorphous state of samples. The scanning electron microscopy, SEM (FEI-SEM Quanta 200 FEG) was used to observe microstructure of the glasses. The Fourier transformation infrared spectroscopy (FT-IR) studies were carried out on the Digilab FTS60s spectrometer in MIR range ( $4000\text{--}400\text{ cm}^{-1}$ ). The samples were prepared in the form of KBr pellets. The micro-Raman spectroscopy study of glasses was carried out on the Raman Jobin-Yvon T-64000 spectrometer, using the  $514.5\text{ nm}$  line of Ar laser ( $30\text{ mW}$ ) for excitant. The spectra were recorded in the  $1400\text{--}200\text{ cm}^{-1}$  range of Raman shifts. Solubility of the glasses was determined using the test applied in agricultural chemistry based on their dissolution in  $2\text{ wt.}\%$  citric acid solution, which simulates the action of organic compounds released by plant roots to extract the useful components from mineral fertilizers [8]. The weight ratio of the glass to the solution was  $1:100$ . Such qualitative proportions of glassy fertilizers to extraction solution simulate conditions of the natural soil environment.

The prepared suspensions of the glass particles in the extraction solution were stirred for  $0.5\text{ h}$  at  $350\text{ r.p.m.}$  speed at  $25^\circ\text{C}$  and then they were filtered. Quantitative analysis of the filtrate was carried out using inductively coupled plasma atomic emission spectroscopy ICP-AES method (OPTIMA 7300DV spectrometer). The filtrate was analyzed by ICP-AES method to determine the amounts of selected elements released from the glass structure to the extraction solution.

### III. Results and discussion

#### 3.1 Glass forming ability

Chemical compositions of the glasses determined by X-ray fluorescence spectrometry (XRF) method is presented in Table 1. The table contains also names of the analysed glasses which will be used in the paper.

XRD results showed (Fig. 1) that glasses with higher  $\text{P}_2\text{O}_5$  content containing less than  $18\text{ mol}\%$  of  $\text{CuO}$  were completely amorphous. In the case of higher content of  $\text{CuO}$  in the structure of these glasses XRD diffractograms revealed the presence of  $\text{Cu}_2\text{O}$  in their structure.

Results of microstructure studies of the glasses with higher content of  $\text{P}_2\text{O}_5$  containing  $6.5\text{ mol}\%$  and  $18\text{ mol}\%$  of  $\text{CuO}$  showed the presence of spherical inclusions in an amorphous matrix (Fig. 2a,b) which in the presence of higher content of  $\text{CuO}$  ( $35\text{Cu6P}$ ) take the form of dendritic crystals of  $\text{Cu}_2\text{O}$  (Fig. 2c).

On the other hand, in the case of glasses with a low  $\text{P}_2\text{O}_5$  content and  $6\text{ mol}\%$  of  $\text{CuO}$  a weak reflex on their diffraction pattern was observed which corresponded to the beginning of  $\text{Cu}_2\text{O}$  crystallization (Fig. 1b).

Thus, the higher content of  $\text{P}_2\text{O}_5$  in the structure of the studied glasses, the higher solubility limit of  $\text{CuO}$ . This behaviour suggested, that copper in the silicate-phosphate glass structure formed  $\text{Cu-O-P}$  bonds.

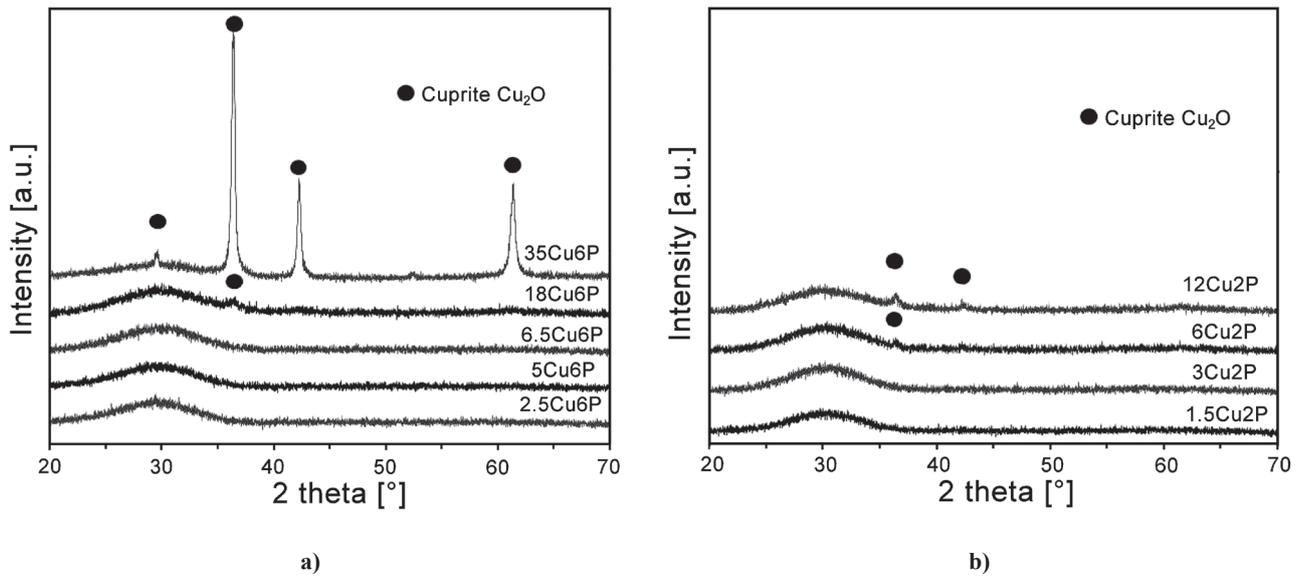
#### 3.2 Spectroscopic study

Effect of copper on the glass structure of the analyzed glasses was evidenced by FT-IR spectra in the middle infrared range (Fig. 3).

FTIR study showed that the bands at  $1030\text{ cm}^{-1}$  and  $1008\text{ cm}^{-1}$  for  $0\text{Cu6P}$  and for  $0\text{Cu2P}$ , respectively, can be assigned to  $\text{Si-O(Si)}$ ,  $\text{P-O}$  and  $\text{Si-O(P)}$  vibrations [9]. Introduction of  $\text{CuO}$  up to  $18\text{ mol}\%$  to the structure of glasses with higher content of  $\text{P}_2\text{O}_5$  causes shift of these bands towards lower wavenumbers, showing a depolymerization effect of copper on the silicate-phosphate framework which was not observed for the glasses with low  $\text{P}_2\text{O}_5$  content.

**Table 1. The chemical composition of the silicate-phosphate glasses from the  $\text{SiO}_2\text{-P}_2\text{O}_5\text{-K}_2\text{O-MgO-CaO-CuO}$  system**

Glass sample	Content of components [mol%]					
	$\text{SiO}_2$	$\text{P}_2\text{O}_5$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{CuO}$
0Cu6P	42.6	6.5	6.7	23	21.2	-
2.5Cu6P	42.6	6.4	6.7	22.8	19	2.5
5Cu6P	43	6.5	6.9	20.3	18.4	4.9
6.5Cu6P	40	7	6.3	16.8	23.9	6.4
18Cu6P	41.7	6.1	6.4	14.6	12.9	18.3
35Cu6P	37.5	5.3	6	7.7	8.4	35.2
0Cu2P	40.2	2.1	6.1	21.3	30.3	-
1.5Cu2P	40.6	2	6	20.5	29.3	1.6
3Cu2P	39.2	2	6.1	20.3	29.2	3.1
6Cu2P	40.6	1.5	6.1	18.6	27.1	6.1
12Cu2P	40.8	2	6.1	15.9	23.2	12.1

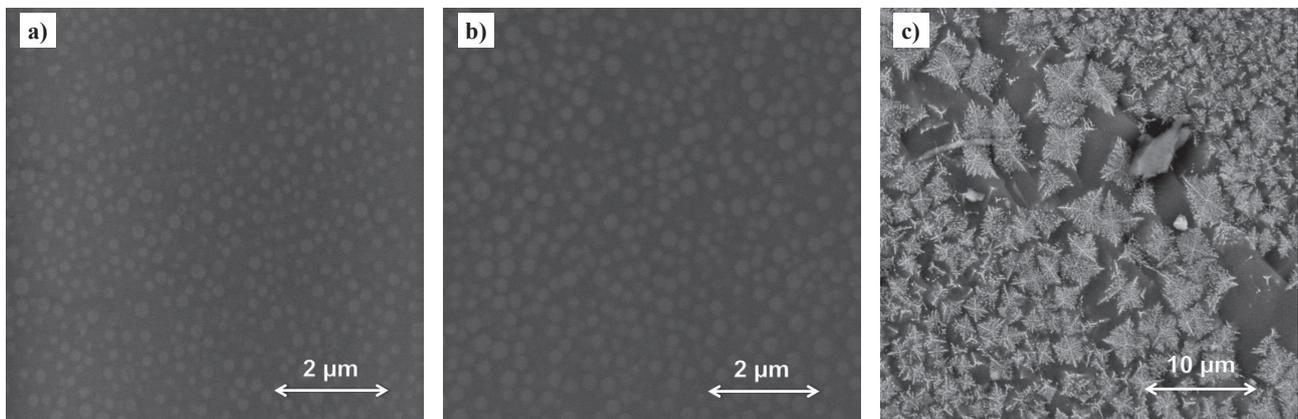


**Figure 1.** XRD patterns of the glasses containing; a) 6 mol %  $P_2O_5$  and b) 2 mol %  $P_2O_5$

Weak band at  $944\text{ cm}^{-1}$  can be attributed to Si-O<sup>-</sup> (broken bonds) vibrations [10]. Furthermore, the introduction of increasing amount of CuO to the structure of analyzed glasses with higher phosphorous content caused a gradual disappearance of this band such behaviour suggested the increasing degree of silicate-phosphate framework polymerization. In the case of glasses with lower content of phosphorous this band was barely noticeable. With the increasing content of CuO in glasses with higher content of  $P_2O_5$  bands at about  $770\text{ cm}^{-1}$  showed tendency to shift towards higher wavenumber. These bands originated from the combination of vibrations of Si-O-Si, Si-O-P and P-O-P bridges and are very weak for glasses with lower content of  $P_2O_5$ . Weak band at about  $557\text{ cm}^{-1}$  which appeared in the FTIR spectra of glasses with higher content of  $P_2O_5$  is characteristic for the bending O-P-O vibrations [10]. There is also weak band at  $476\text{ cm}^{-1}$  partially overlapping with the above mentioned originating from the combination of vibrations of O-Si-O and O-P-O bonds. The increasing amount of CuO in the structure of these glasses caused shift of the above mentioned band towards lower wave-

numbers. On the spectra of glasses with lower content of  $P_2O_5$  there is only one band in the lower range of wavenumbers with the maximum at  $513\text{ cm}^{-1}$  which originated from the combination of vibrations of O-Si-O and O-P-O bonds, but with the increasing amount of CuO in the glass structure this band shifted towards lower wavenumber showing a depolymerization effect of copper on the silicate-phosphate glass network.

The effect of copper as the glass modifier on structure of glasses with higher content of  $P_2O_5$  was also evidenced by Raman spectra (Fig. 4). They were characterized by bands at  $960$  and  $1070\text{ cm}^{-1}$  which could be assigned to Si-O<sup>-</sup> stretching vibrations in Q<sup>2</sup>, Q<sup>1</sup> (at  $960\text{ cm}^{-1}$ ) and Q<sup>3</sup> (at  $1070\text{ cm}^{-1}$ ) units in the silicate network. The effect of copper addition on this part of the spectrum was not very noticeable. On the other hand, the very weak band at  $454\text{ cm}^{-1}$  for 0Cu6P glass sample could be attributed to symmetric stretching of O-P-O bending modes of the orthophosphate PO<sub>4</sub><sup>3-</sup> units (Q<sup>0</sup>) which shifted towards lower wavenumber with the increasing content of CuO in the glass structure, indicating depolymerization of the phosphate network [11].



**Figure 2.** SEM microphotographs of: a) 6.5Cu6P, b) 18Cu6P and c) 35Cu6P samples

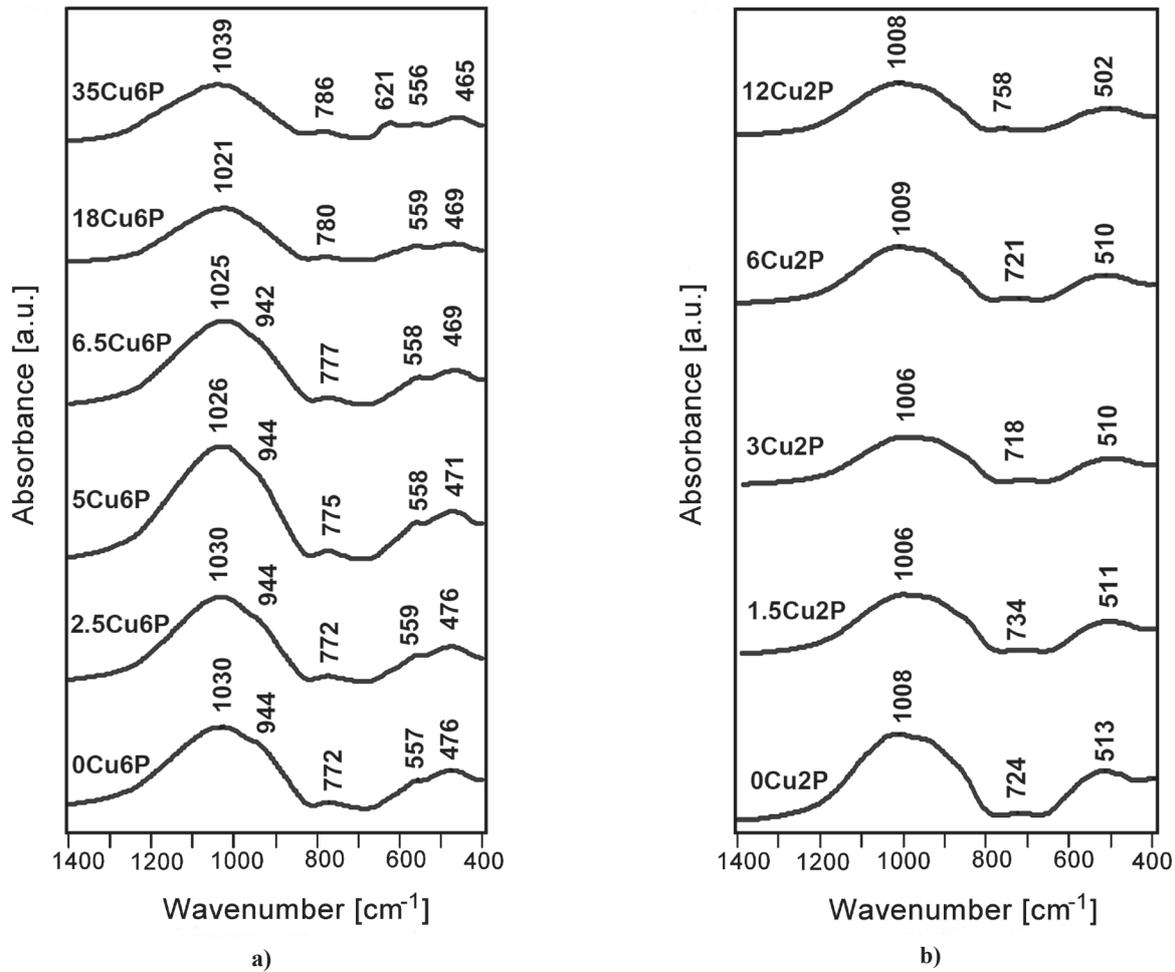


Figure 3. FT-IR spectra of the silicate-phosphate glasses with a) 6 mol % and b) 2 mol% of P<sub>2</sub>O<sub>5</sub> content

Band at 588 cm<sup>-1</sup> for the 0Cu6P glass sample which is sharper than the previous one could be attributed to the symmetric stretching of P-O<sup>-</sup> bonds of the orthophosphate units (Q<sup>0</sup>). This band becomes more distinct with the increasing content of CuO in the structure of analyzed glasses.

The spectroscopic studies confirmed that some changes around P-O-P bonds in the structure of the considered glasses took place. They might be related to formation of P-O-Cu bonds. Formation of such bonds can be explained based on the difference of the ionicity of bonds in the oxygen bridge ( $\Delta i_G$ ), which can be used to measure local chemical affinity of cations to oxygen in the oxygen bridge. The higher is its value, the greater is the local chemical affinity of cations to the bridging oxygen [12].

Thus the presence of copper in the structure of the studied glasses caused a break of P-O-P bonds rather than Si-O-Si bonds due to its greater affinity to phosphorus than to silicon ( $\text{Cu}^{2+}\text{-O-P } \Delta i_G = 0.303 > \text{Cu}^{2+}\text{-O-Si } \Delta i_G = 0.189$ ,  $\text{Cu}^+\text{-O-P } \Delta i_G = 0.449 > \text{Cu}^+\text{-O-Si } \Delta i_G = 0.335$ ).

### 3.3 Chemical activity

The amounts of selected chemical components released from the examined glasses structure in the 2 wt.% citric acid solutions as determined by the ICP-AES method are shown in Fig. 5. The results are pre-

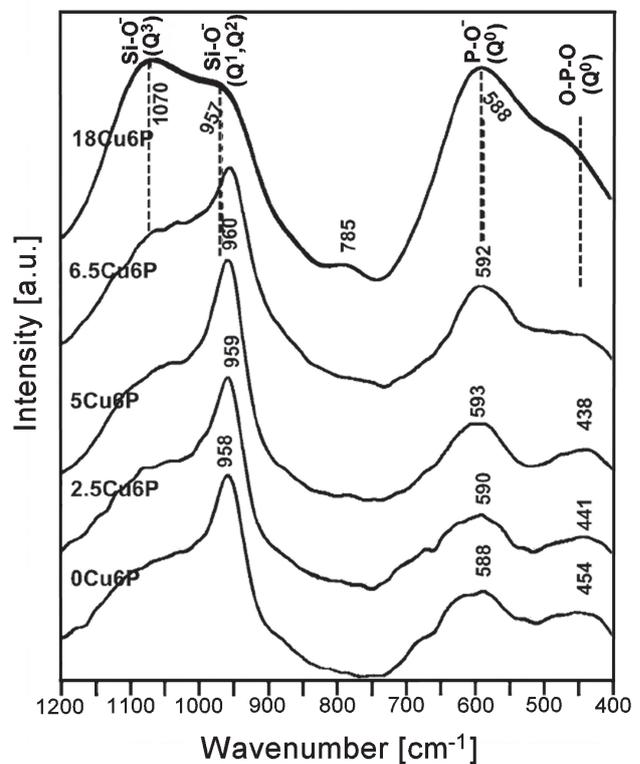


Figure 4. Raman spectra of the silicate-phosphate glasses with 6 mol% P<sub>2</sub>O<sub>5</sub> content

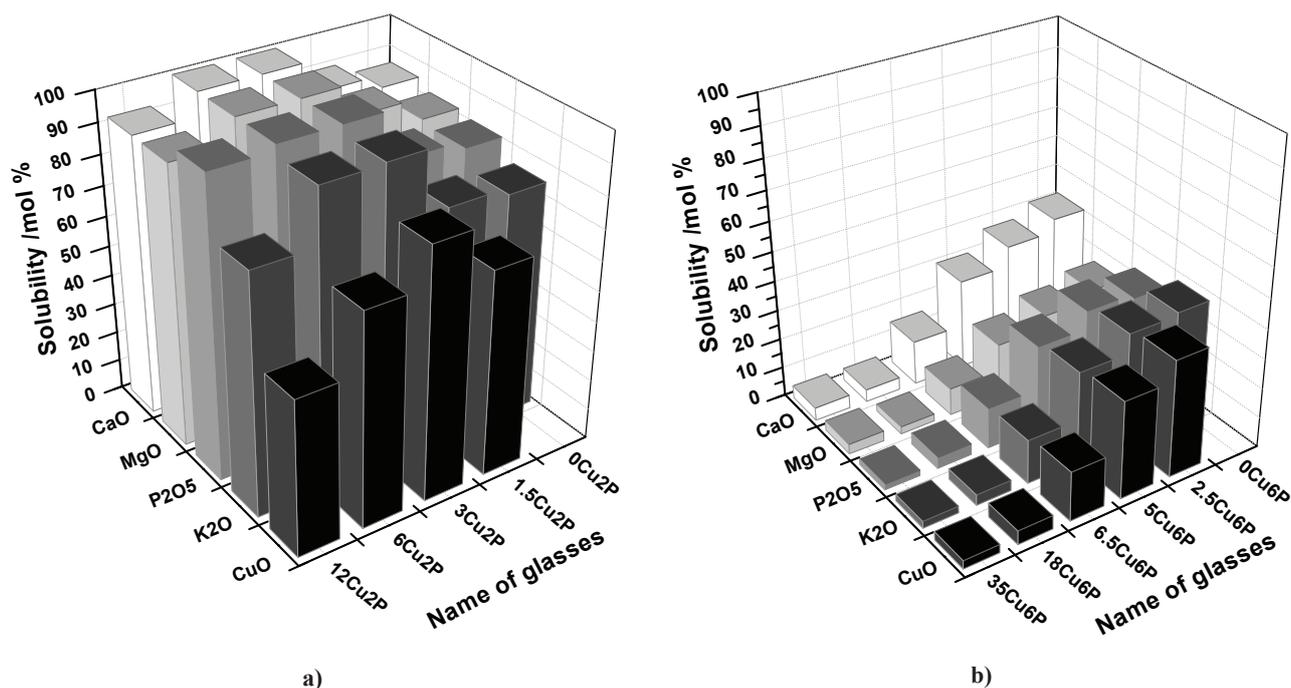


Figure 5. Solubility of chemical components of silicate-phosphate glasses in 2 wt.% citric acid solutions with a) 2 mol% and b) 6 mol% of P<sub>2</sub>O<sub>5</sub> content

sented in molar fraction of a given compound (oxide) introduced to the glass batch.

The solubility studies indicate that introduction of increasing amount of CuO into the structure of the glasses with higher content of P<sub>2</sub>O<sub>5</sub> distinctly decreases its solubility. During “in vitro” experiments about 40 mol% of the initial components content like P<sub>2</sub>O<sub>5</sub>, CaO, K<sub>2</sub>O, CuO dissolves from the glass containing 2.5 mol% of CuO, while glass containing 18 mol% of CuO releases only about 4 mol% of their components (Fig. 4b). In the case of glasses with lower content of P<sub>2</sub>O<sub>5</sub>, the introduction of even small quantity of CuO (1.5 mol%) into their structure increases the solubility of macroelements which they are containing. About 70–100 mol% of the initial macrocomponent content dissolves from the glass containing lower content of P<sub>2</sub>O<sub>5</sub> and 3 and 6 mol% of CuO (3Cu2P and 6Cu2P glasses, respectively) in contrast to the glasses containing 6 mol% of P<sub>2</sub>O<sub>5</sub> which released less than 40 mol% of their components.

According to structural studies presented earlier, such behaviour of the examined glasses resulted from the changes of kind of bonds formed in the considered glasses. In the structure of glasses with higher content of P<sub>2</sub>O<sub>5</sub>, the increasing amount of CuO results in the formation of increasing amount of chemically stable P-O-Cu bonds which in turn decrease solubility of the glasses.

#### IV. Conclusions

Copper plays an important role as a microelement that is necessary in the growth process of plants. Sil-

icate-phosphate glasses with copper addition find application as glassy carriers of this microelement. On the basis of XRD, SEM, FTIR and Raman spectroscopy studies, the influence of copper addition on the structure of silicate-phosphate glasses was evaluated.

It was found that the increasing content of phosphorous caused increase of solubility of copper during the melt quenching of the studied glasses which was the result of formation of P-O-Cu instead of P-O-P bonds. Along with the copper and phosphorous content increase in the glass structure, the amount of P-O-Cu bonds increases. Formation of chemically stable P-O-Cu bonds decreases glass solubility in the extracting solution simulating the soil environment conditions.

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