



# Influence of CuO and ZnO addition on the multicomponent phosphate glasses: Spectroscopic studies



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## ABSTRACT

The spectra of phosphate-silicate glasses from the P<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>–K<sub>2</sub>O–MgO–CaO system modified with the addition of CuO or ZnO have been studied by means of FTIR, Raman and <sup>31</sup>P MAS NMR spectroscopy. All glasses were synthesized by the conventional melt-quenching technique and their homogeneous chemical composition was controlled and confirmed. By using the aforementioned research techniques, the presence of structural units with various degrees of polymerization was shown in the structure of analyzed phosphate-silicate glasses: Q<sup>3</sup>, Q<sup>2</sup>, Q<sup>1</sup> and Q<sup>0</sup>. It was found that an increase in the content of CuO or ZnO in the composition of analyzed glasses, which are introduced at the expense of decreasing amounts of CaO and MgO, has a different influence on the phospho-oxygen network. It was shown that copper ions cause its gradual polymerization, while zinc ions cause its depolymerization. At the same time, polymerization of the silico-oxygen subnetwork was found. Additionally, in the case of glasses containing increasing amounts of ZnO, a change of the role of zinc ions in the vitreous matrix was confirmed (from the modifier to a structure-forming component).

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## 1. Introduction

Phosphate glasses are an interesting material especially in connection with their diverse applications. They include: sealing materials, medical use and solid-state electrolytes [1], but also containment of radioactive waste [2], as degradable tissue and bone scaffolds within the human body [3] and agro-fertilizers with controlled solubility [4,5]. Such a broad range of phosphate glass applications results from the possibility of broad modifications of their chemical composition.

It is known that the structure of phosphate glasses consists of a 3-dimensional network of corner-sharing PO<sub>4</sub> tetrahedra, each of which is connected with a non-bridging P=O bond. This oxygen atom does not take part in the formation of polymerized phosphate anions as it does not build P–O–P oxygen bridges. It can, however, form bonds with a modifier cation, which results in the formation of Me–O–PO<sub>3</sub> bonds, where Me is the modifier cation (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Cu<sup>+</sup>, Zn<sup>2+</sup>, K<sup>+</sup>) [6]. The gradual introduction of growing amounts of modifying oxides into the structure of phosphate glasses usually results in their gradual depolymerization.

In recent years, phosphate glasses modified by the addition of zinc and copper ions have enjoyed a great interest as they find unconventional applications as carriers of macro- and microelements, which are necessary for proper development of plants.

It is known from literature data that copper plays the role of a modifier in the phosphate structure [7–9]. Depending on the ZnO content in the structure of glasses, the structural role of ZnO in many oxide glasses is unique since zinc oxide can act both as a glass former and a glass modifier. As a glass former, ZnO enters the network with ZnO<sub>4</sub> structural units. As a network modifier, zinc ion is octahedrally coordinated and behaves like conventional alkali oxide modifiers [10].

Numerous literature reports show that both in two-component CuO–P<sub>2</sub>O<sub>5</sub> [8] and three-component systems P<sub>2</sub>O<sub>5</sub>–Na<sub>2</sub>O–CuO [9,10] copper gradually introduced at the expense of P<sub>2</sub>O<sub>5</sub> or Na<sub>2</sub>O influences progressing depolymerization of the vitreous structure, which is manifested by gradual transformation of the three-dimensional network formed from phosphorus-oxygen tetrahedra (type Q<sup>3</sup>) to the metaphosphate chain structure, which is formed from phosphorus-oxygen units of the Q<sup>2</sup> type. Such results of research were obtained using FTIR, Raman, XPS [7] spectroscopy methods as well as <sup>31</sup>P MAS NMR [8]. It results from them that an increase in the CuO addition in the structure of phosphate glasses

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influences the formation of P–O–Cu bonds, which gradually replace P–O–Na bonds, which is accompanied by an increase in the density of the glasses under analysis. Similar research results are presented in Ref. [12].

Equally comprehensive literature data can be found for phosphate glasses modified by an increasing amount of ZnO. The authors of studies [13–15] agree on the influence of zinc ions on the structure of two-component glasses from the  $P_2O_5$ –ZnO system, which are introduced in small amounts (up to 0.8% mol) to the chemical composition of tested glasses. Using Raman and  $^{31}P$  MAS NMR spectroscopies, they showed that an increase in the ZnO content in their chemical composition initially influences a decrease in the phosphorus-oxygen units of the  $Q^3$  type with a simultaneous increase in the phosphorus-oxygen units of the  $Q^2$  type. A further increase in the ZnO content in the structure of the aforementioned glasses influenced further depolymerization of their structure and larger amounts of structural units of the  $Q^1$  type and isolated units of the  $Q^0$  type. The influence of larger amounts of ZnO on the structure of phosphate glasses was analyzed in Refs. [16], in which 46% mol ZnO was introduced into the glass composition. Also, with such a considerable ZnO content, information about its depolymerizing influence on the structure of considered glasses was obtained, which was registered in the form of the decreasing part of phosphorus-oxygen units of the  $Q^2$  type at the expense of the increasing share of units of the  $Q^1$  and  $Q^0$  type. The simultaneous increase in the number of non-bridging oxygen atoms was also emphasized. The research obtained by the Authors was previously confirmed by NMR and XPS examinations [17].

It should be emphasized that there is scarce information on the influence of selected transition elements on the structure of phosphate glasses containing a small amount of another structure-forming component in the form of  $SiO_2$ . The literature provides the influence of molybdenum ions on the structure of glasses from such a system [18,19]; however, the influence of manganese ions [20] and zinc ions [21] was analyzed only in terms of their thermal characteristics. Therefore, for the purposes of this study, research was undertaken with a view to explaining both the influence and the role of the growing amount of CuO and ZnO on the structure of multicomponent glasses from the  $P_2O_5$ – $SiO_2$ – $K_2O$ – $MgO$ – $CaO$  system. The following spectroscopic methods were used for this purpose: FTIR, Raman and  $^{31}P$  MAS-NMR. The possibility of using such multicomponent glasses as a new generation of fertilizers with a controlled, slow release rate of the nutrients for plants, should also be emphasized.

## 2. Experimental

A homogenous phosphate-silicate glasses from the  $P_2O_5$ – $SiO_2$ – $K_2O$ – $MgO$ – $CaO$  system with increasing contents of ZnO and CuO were prepared. The glasses were produced by traditional melting of raw materials mixture, i.e.  $(NH_4)_2HPO_4$ ,  $SiO_2$ ,  $K_2CO_3$ ,  $MgO$ ,  $CaCO_3$ , CuO and ZnO at 1100 °C. Amorphous state of glasses was confirmed using the X-ray diffraction method (X'Pert PRO Diffractometer, Philips) and the chemical composition of chosen glasses was controlled by X-ray fluorescence spectroscopy using ARL Advant XP spectrometer, the results are shown in Table 1.

FTIR spectroscopic measurements of the glasses were conducted with a Bruker Vertex 70v spectrometer using the transmission mode and spectra were registered with absorbance scale. The samples had the form of pellets made of the glasses mixed with KBr. Spectra were collected after 124 scans with 4  $cm^{-1}$  resolution. Positions of bands on the MIR spectra were determined automatically by Win-IR software.

Raman studies were carried out using Horriba Yvon Jobin Lab-

RAM HR micro-Raman spectrometer equipped with a CCD detector. Excitation wavelength of 532 nm was used and beam intensity was about 10 mW. Acquisition time was set to 30 s. The position of bands on the Raman spectra was defined automatically in Win-IR.

The local glass structure was investigated using  $^{31}P$  MAS NMR spectroscopy. The solid state  $^{31}P$  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  $^{31}P$  measurements, respectively. A single 3  $\mu s$  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. A 50 Hz Lorentzian line broadening was applied to the spectra, which was equal to about 0.4 ppm for the phosphorus. The frequency scale in ppm was referenced to TMS and 85 mol%  $H_3PO_4$  for the  $^{31}P$  spectra.

## 3. Results and discussion

### 3.1. FTIR spectroscopy

FTIR spectra of the tested phosphate glasses are presented in Fig. 1. FTIR spectra of all discussed glasses modified with the addition of CuO or ZnO (Cu41P or Zn41P) show considerable similarity. They are characterized by the presence of three main absorption bands with maxima located within the following waveform ranges: 1400–1200, 1200–850, 800–650 and 650–400  $cm^{-1}$ . It should be noted that the conventional Q-site notion was used in the interpretation of the results [22].

#### 3.1.1. 1400–1200 $cm^{-1}$ range

Within this wavenumber range, one band is present in FTIR spectra of analyzed glasses from the maximum at approx. 1280  $cm^{-1}$ . Literature data [23,24] report that their presence is related to doubly bonded oxygen vibration  $\nu_{as}(P=O)$  modes and/or anti-symmetrical vibrations of  $PO_2^-$  groups (in  $Q^2$  units). A small addition of CuO or ZnO (2% mol) introduced at the expense of the CaO and MgO content does not change the location of these bands. The introduction of larger amounts of CuO into the composition of these glasses does not result in a shift in their location towards lower wavenumber values (from 1285 to 1276  $cm^{-1}$ ). An increase in the ZnO content in an amount of up to 15% mol did not cause a change in the position of the band under analysis, while the addition of 30 mol% of this ingredient contributed to a significant shift of its position towards lower wavenumber values (approx. 1282  $cm^{-1}$ ).

Such behaviour implies that both CuO and ZnO, introduced at the expense of MgO and CaO result in the breaking of P=O bonds and the formation of bonds of the P–O–Cu or P–O–Zn type. At the same time, it should be emphasized that for glasses from the Zn41P group, the discussed effect implies a stronger impact of copper ions on the phosphorus-oxygen subnetwork.

#### 3.1.2. 1200–850 $cm^{-1}$ range

Three further bands situated at approx. 1100, 1000 and 900  $cm^{-1}$  (1200–850  $cm^{-1}$ ) for both groups of glasses (Cu41P and Zn41P) were assigned to the next range of wavenumbers.

The first of these is assigned to the combination of P–O and Si–O stretching vibration of combination of P–O–P and P–O–Si bridging (in  $Q^2$  units) [25]. With higher CuO (15–30 mol%) or ZnO (30 mol%) content in the glass composition, their location moves towards lower wavenumbers; it is particularly visible for 30Cu41P glass. On this basis, conclusions are drawn about a depolymerizing influence of copper and zinc ions on the phosphate-silicate

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