

# THE INFLUENCE OF Cu, Ca AND Zn ON THE PROPERTIES OF METAPHOSPHATE GLASSES

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*Metaphosphate glasses  $ZnCu_{(1-a)}(PO_3)_2$  and  $Ca_bCu_{(1-b)}(PO_3)_2$  were prepared with the aim of studying the effect of different cations on solubility in water, on volume homogeneity and on the thickness of the surface layer. The relative ionicity of the Me-O(-P) bond (Me = Zn, Ca, and Cu) was determined using relative polarizability obtained by analyzing the Raman spectra. It was determined that the relative ionicity, i.e. the polarity of the bond, increases from the Cu donor-acceptor bond through the relatively covalently bound Ca to the significantly polar Zn bond. Compared to copper, both zinc and calcium reduce the compactness of the glass structure, of course to a different extent, and thus affect the coefficient of thermal expansion as well as the glass transition temperature. As can be expected, both from the relative ionicity and the effect on the compactness of the structure, the greatly increased solubility of glasses in water when replacing copper with calcium or zinc confirmed the reality of the conclusions about their influence on the properties of glasses. By dissolving glasses in water, the thicknesses of the surface layers were determined, which increases significantly from copper to calcium to zinc. Furthermore, phase segregation in the glass volume was identified.*

## INTRODUCTION

Phosphate glasses are widely studied materials due to a number of unique properties, such as low synthesis temperature, low glass transition temperature, low melt viscosity, UV permeability or the higher thermal expansion coefficient as well as biocompatibility [1-3]. From a technological point of view, phosphate glasses have emerged as promising for amplifiers and lasers, channel waveguide lines, photonics, optical data storage and glass to melt seals [4-6]. Its major advantage in the field of medicine lies precisely in its composition, which is very similar to bone. The phosphate glass and its composites could be used to fix fractures or regenerate bones and cartilage or as an alternative to the current methods available for the treatment of infections [7-9].

Transition metals, embedded in a phosphate glass network, significantly improve the various important properties of glass, such as their mechanical strength, chemical durability, hardness and optical properties [10, 11]. Transition metal ions usually occur in glasses

in multiple oxidation states, and the movement of charge carriers from a lower to a higher valence state makes glasses conductive [12]. Compared to silica and borate glasses, phosphate glasses can accommodate higher concentrations of transition metal ions without crystallization [13].

Copper is one of the important transitional elements giving specific properties to glass materials. Copper can be found in glasses as cuprous Cu(I) or cupric Cu(II) ions in the form of a network modifier or metallic nanoparticle [14]. Cu(II) can be reduced to Cu(I), especially using  $NH_4H_2PO_4$  as the starting compound, i.e. moderate reducing conditions [15-17]. Copper phosphate glasses have interesting electrical and optical properties and have been of interest for their potential use as super-ionic conductors, solid state lasers, color filters and materials for non-linear optics [17, 18]. These glasses have also been developed for potential applications in medicine, such as wound healing applications because of the antibacterial properties of copper [19].

The structure and properties of binary copper-phosphate glasses were studied using Raman spectroscopy, FTIR and UV-Vis-NIR spectroscopy. The  $\text{Cu}^{2+}$  in an octahedral coordination with a strong tetragonal distortion has been found to be responsible for coloration of glasses [16]. The authors also found that the color of the glasses is further affected by the optical absorption bands of  $\text{Cu}^+$  partly extended into the visible region. The differing local structures of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions result in a variation of the Raman spectra of the binary glasses [20]. These ions also exhibit different intermolecular forces and the glass transition temperature of the copper metaphosphate glass was found to increase with the increasing  $[\text{Cu}^{2+}]/[\text{Cu}]_{\text{total}}$  ratio [15].

Systematic studies have recently been conducted on the effect of copper on the structure and properties of ternary  $\text{Na}_2\text{O}-\text{CuO}-\text{P}_2\text{O}_5$  glasses. It was found that copper ions significantly crosslink phosphate chains, which results in an increase in  $T_g$  and hardness. The emerging P-O-Cu bonds are more hydration resistant and bring about an improvement in chemical durability [2, 21, 22].

Zinc phosphate glasses are of interest due to their good hardness, mechanical resistance, chemical durability, while maintaining a low glass transition temperature [23-25]. Their low melting point is an excellent property for various technological applications such as molded contact lenses or sealing glasses [24]. It was found that zinc occurs in a glass system with coordination numbers 4 and 6 varying according to the zinc content [26, 27].

Copper-zinc phosphate glasses were studied by infrared specular reflection spectroscopy [28]. Their glassy structure is affected by the ratio of metal oxide to  $\text{P}_2\text{O}_5$  but is independent of the ZnO/CuO ratio which was explained by the similarity of the ionic radii of copper and zinc. The switching properties of glass system  $x\text{CuO}-(50-x)\text{ZnO}-50\text{P}_2\text{O}_5$  were investigated in [29]. Copper zinc phosphate glasses have been also developed for potential uses in medicine because of their antibacterial properties [4, 30].

Calcium can only be present in glass in the form of Ca(II) and causes crosslinking of the glass structure, which manifests itself in an increase in the chemical and mechanical resistance of the glass [31]. Calcium phosphate glasses are attractive materials for optics [32] and can also be used as potential biomaterials for use as temporary bone substitutions [33]. The ternary glass system  $x\text{CuO}(1-x)[\text{P}_2\text{O}_5 \cdot \text{CaO}]$  with  $0 \leq x \leq 40$  mol. % was investigated by EPR and Raman spectroscopy [34]. The results of EPR analysis indicate a tetrahedral symmetry for Cu(II) in the studied glasses. The local environment in alkaline earth metaphosphate glasses was studied by ESR and UV-visible spectroscopy in [35]. It was found that  $\text{Cu}^{2+}$  has an octahedral environment with tetragonal distortion increasing from  $\text{Ba}(\text{PO}_3)_2$  to  $\text{Mg}(\text{PO}_3)_2$ .

In our previous work, the binding possibilities of calcium, zinc and copper in metaphosphate glasses of the two series  $x\text{ZnO}-(50-x)\text{CuO}-50\text{P}_2\text{O}_5$  and  $y\text{CaO}-(50-y)\text{CuO}-50\text{P}_2\text{O}_5$  were studied by Raman spectroscopy,  $^{31}\text{P}$  MAS NMR and EPR [36]. Using those methods, it was found that zinc and copper are four coordinated and interact with donor oxygen in the same phosphate chain, while the coordination number of Ca(II) is six and it crosslinks the phosphate chains. An analysis of the shift of vibrational energies found that the bond strength decreases in the order  $\text{Zn-O} > \text{Cu-O} > \text{Ca-O}$ . In copper-containing glasses, the presence of two metaphosphate phases with different degrees of ordering was demonstrated by means of  $^{31}\text{P}$  MAS NMR.

This paper builds on our previous work [36] and follows up on the study of glasses of two composition series mentioned above. The aim of this work was to determine the density, coefficient of thermal expansion, glass transformation temperature for the studied glasses and further study the solubility of these glasses in water with the aim of determining the thickness of the surface layer of virgin glass and obtaining information about bulk glass homogeneity. The solubility study method used in this work differs from commonly used methods in that virgin samples are used, the surface or geometry of which is not modified in any way and therefore, for example, the surface is not mechanically damaged and thus no fault conditions are artificially created that necessarily affect the interaction of the surface with solvent molecules. It is therefore a study of the solubility of glasses with a surface that was created during the cooling of the glass-forming melt, i.e. with a surface when the glass-forming melt reached the minimum achievable change in Gibbs energy. The correlation of all the obtained experimental results with the properties of both the glass-forming network and metal cations are discussed.

## EXPERIMENTAL

Two glass series  $x\text{CuO}-(50-x)\text{ZnO}-50\text{P}_2\text{O}_5$  ( $x = 0, 1, 5, 10, 15, 20, 30, 40$  and  $50$ )  $y\text{CuO}-(50-y)\text{CaO}-50\text{P}_2\text{O}_5$  ( $x = 0, 2, 5, 10, 20, 30, 40, 45$  and  $50$ ) were prepared from  $\text{CuO}$ ,  $\text{ZnO}$ ,  $\text{CaCO}_3$  and 85 %  $\text{H}_3\text{PO}_4$  of high reagent grade purity (Sigma-Aldrich) using the conventional melt-quenching technique. The synthesis was carried out in platinum crucibles and firstly, the mixture of oxides and phosphoric acid was calcined in the temperature interval from 250 to 700 °C. The batches were then melted in an electric furnace for 10 min at a temperature range of 1180 – 1250 °C, the synthesis temperature being dependent on the increasing amount of copper. The melt was poured into a graphite mold, preheated at ~350 °C. The glass was then left to cool to room temperature.

The amorphous character of all the glasses was confirmed by powder X-ray diffraction (XRD) using a D8 Advance diffractometer (Bruker), Cu K( $\alpha$ ) radiation. The chemical composition of the prepared glasses was checked with micro-X-ray fluorescence ( $\mu$ -XRF) analysis on a M4 Tornado (Bruker) analyzer using a standardless analysis as part of the spectrometer software.

Raman spectra were measured on bulk samples at room temperature using Raman confocal microscope LabRam HR (HORIBA Jobin Yvon) in back-scattering geometry under excitation with Nd:YAG laser 532 nm. For correction of the temperature dependent population of phonon levels, the intensities of Raman spectra were reduced using the Gammon–Shuker relation [37] and then the baselines were corrected. The obtained data were analyzed using LabSpec 5 (Horriba Jobin-Yvon) software.

$^{31}\text{P}$  MAS NMR spectra were collected at room temperature on an Ascend 500 spectrometer (Bruker) with a 11.74T magnet and 3.2 mm probe ( $^{31}\text{P}$  Larmor frequency = 202.40 MHz).  $^{31}\text{P}$  MAS NMR was performed using a single pulse excitation and spin rate 15 kHz, pulse length 2.4  $\mu\text{s}$ , power level 56 W and recycle delay 60 s.  $(\text{NH}_4)_2\text{HPO}_4$  was used as a secondary standard (0.90 ppm). The measured data were analyzed with TopSpin 3.2 software (Bruker).

The density of the glasses was determined with an accuracy of  $\pm 1 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$  using the standard Archimedean method with toluene as the immersion liquid ( $\rho = 0.8669 \text{ g} \cdot \text{cm}^{-3}$ ).

The dilatometric glass transition temperature and the thermal expansion coefficient,  $\alpha$ , were obtained by thermomechanical analyzer TMA Q400 (TA Instruments). The measurements were collected under nitrogen atmosphere (flow rate 20  $\text{ml} \cdot \text{min}^{-1}$ ) using an expansion probe with a load force of 0.050 N and a heating rate of 10  $^\circ\text{C} \cdot \text{min}^{-1}$ .

The solubility of metaphosphate glasses was studied on freshly prepared glasses with the original untreated surface. The prepared glasses were optically homogeneous therefore the density can be assumed as constant in the whole volume. Glass samples resembling a spherical canopy as much as possible were selected as representative samples. Before dissolution, the samples were weighed with an accuracy 0.01 mg and using a digital micrometer measured with an accuracy 0.01 mm. The sample volume was then calculated using the experimentally determined density, both at the beginning of the experiment and at all the time intervals used. It is clear that the thickness of the dissolved layer for a given time interval is so small that it cannot be measured directly. However, since the actual volume of the sample in each time interval is known, the dissolved layer loss,  $\Delta d$ , based on the known geometry of the dissolved body, can be determined. From the obtained results, the rate of dissolution and the rate of the etched layer loss can be

calculated. This method of determining the thickness of the dissolved layer has already been successfully used [38]. Glass samples were immersed in 100 ml of distilled water (pH = 6.8) in 250 ml Erlenmeyer flasks closed with a rubber stopper and shaken at ambient temperature by a laboratory shaker. Placing the flasks on a shaker prevents irregular dissolution of the surface of the samples. At the indicated time intervals, the individual samples were removed from the flask, dried and weighed, again with an accuracy 0.01 mg. After each weighing, the water was replaced to avoid the formation of a phosphate solution. The thickness of the dissolved layer was determined from the difference in weight using the Solver Excel, which reflects the current volume, the decreasing surface area of the samples and the constant density of the prepared glasses.

## RESULTS AND DISCUSSION

### Characterization of glasses

Two glass lines  $x\text{ZnO}-(50-x)\text{CuO}-50\text{P}_2\text{O}_5$  and  $y\text{CaO}-(50-y)\text{CuO}-50\text{P}_2\text{O}_5$  have been prepared, that is, glasses whose chemical composition can be expressed as  $\text{Zn}_a\text{Cu}_{(1-a)}(\text{PO}_3)_2$  and  $\text{Ca}_b\text{Cu}_{(1-b)}(\text{PO}_3)_2$ , where  $a = x/50$  and  $b = y/50$ . The prepared samples were optically homogeneous and their glassy character was confirmed by XRD and the chemical composition of the prepared glasses was precised by  $\mu$ -XRF analysis. The deviations from the nominal composition, expressed in oxides, were found to be less than 1 mol. %, therefore starting batch compositions are used in further discussion.  $\mu$ -XRF analysis and concentration of spins, obtained by EPR spectroscopy, clearly indicate that copper(2+) was not reduced during the synthesis and all copper is present as  $\text{Cu}^{2+}$ , see also [36].

Common glass for both lines, copper metaphosphate, is colored dark green, while, of course, the terminal glassy zinc and calcium metaphosphates are colorless. As the content of copper decreases, the color of the prepared glasses changes from dark green to light blue.

### Structure of the glasses

The basic structural information obtained by Raman spectroscopy,  $^{31}\text{P}$  MAS NMR and EPR are discussed in detail in our previous paper [36]. Further analysis of Raman and  $^{31}\text{P}$  MAS NMR spectra, carried out as part of this work, provided additional results which are presented below.

The selected Raman spectra of both series, Figure 1, clearly confirm that the metaphosphate network was preserved. The Raman spectra were newly analyzed from the point of view of bond ionicity, which can be assessed based on the well-known fact that the intensity of Raman bands is a function of bond polarizability. In case of an ionic bond, the increase in partial charges at the ends of the bonds fixes the electron density during

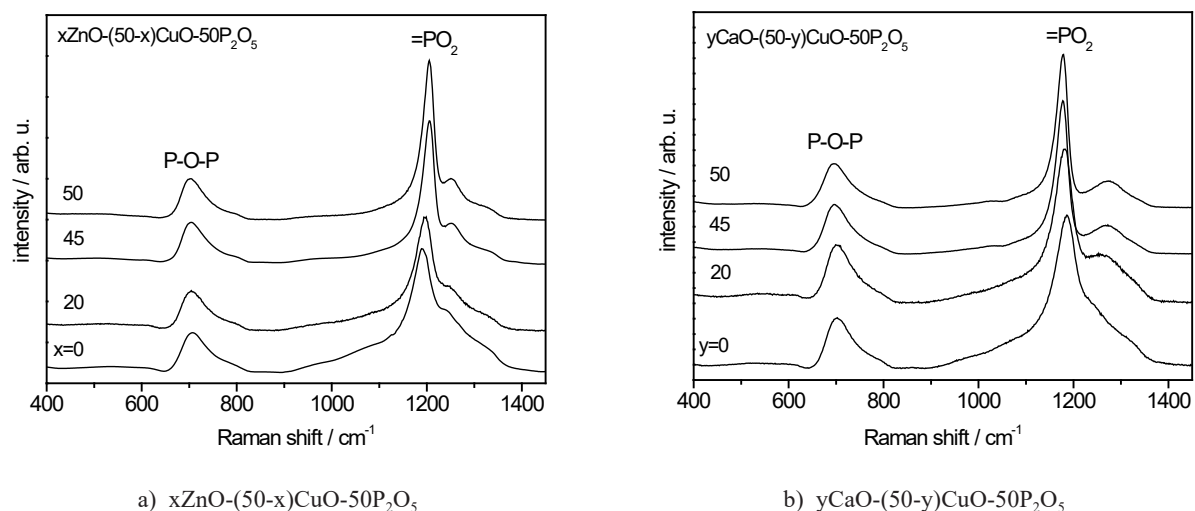


Figure 1. Selected Raman spectra of both glass series.

the vibrational motion and thus the change of bond polarizability decreases as the ionicity of the bonds increases.

All three metals(+II) interact with the non-bridging oxygens of the metaphosphates by forming a polar covalent bond. The information about the relative ionicity can be obtained by integrating the Raman spectra in the region of non-bridging oxygen vibrations, i.e. around  $1200\text{ cm}^{-1}$ . To obtain semi-quantitative information, the spectra were normalized to the same integral intensity of the asymmetric band of bridging oxygen vibration, centered at  $\sim 700\text{ cm}^{-1}$ . The degree of ionicity then corresponds to the integral intensity in the vibrational region of non-bridging oxygen. To determine the relative ionicity of the bonds, when Cu is replaced by zinc or calcium, the integral intensity of Cu-O(-P) bond in the copper-meta phosphate was set to zero and subsequently, the relative ionicity of Zn-O(-P) and Ca-O(-P) bonds were normalized from 0 to 1, Figure 2. It should be noted at this point that this in no way means that the ionicity

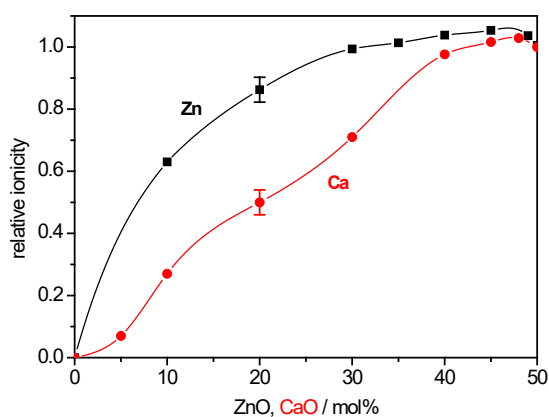


Figure 2. The compositional dependence of relative bond ionicity change of both studied series glasses.

of Zn-O(-P) and Ca-O(-P) is the same. The graph only expresses the compositional dependence of relative ionicity. The increase in ionicity of the Zn-O(-P) bond is significantly faster compared to the Ca-O(-P) bond, which means that the Ca-O(-P) bond has a more covalent character than the Zn-O(-P) bond.

The relative ionicity can subsequently be correlated with the solubility of the glasses, as will be discussed later.

$^{31}\text{P}$  MAS NMR spectra were discussed in the previous work [36], confirming the presence of metaphosphates with a small amount of pyrophosphates (about 4 %). Of particular interest is the coexistence of two metaphosphate phases labeled  $Q^{21}$  and  $Q^{22}$ .  $Q^{22}$  phase containing most of the copper(+II), whose paramagnetism shifts the  $^{31}\text{P}$  MAS NMR resonance to the region of higher magnetic fields and the larger half width of the resonance band compared to the  $Q^{21}$  one indicates a relatively greater disorder of the  $Q^{22}$  phase. The formation of these two phases is clearly caused by the copper ions, since Cu-free glasses are formed only by the single  $Q^{21}$  phase and the content of the less ordered phase  $Q^{22}$  increases with increasing copper concentration. It was also found that not only copper but both zinc and calcium ions are also partially present in this phase [36].

Subsequent detailed analysis revealed that zinc and calcium have significantly different effects on the structure of copper metaphosphate glasses, as shown by the compositional dependence of the ratio of both metaphosphate structures, see Figure 3. It is clear that in both series of glasses, with increasing content of zinc or calcium ions, the content of structural units  $Q^{22}$  decreases at the expense of structural  $Q^{21}$  units. Binary glasses  $50\text{ZnO}-50\text{P}_2\text{O}_5$  and  $50\text{CaO}-50\text{P}_2\text{O}_5$  are formed exclusively by the more ordered metaphosphate  $Q^{21}$  phase, in contrast to copper phosphate glass,  $50\text{CuO}-50\text{P}_2\text{O}_5$ , where surprisingly the less ordered



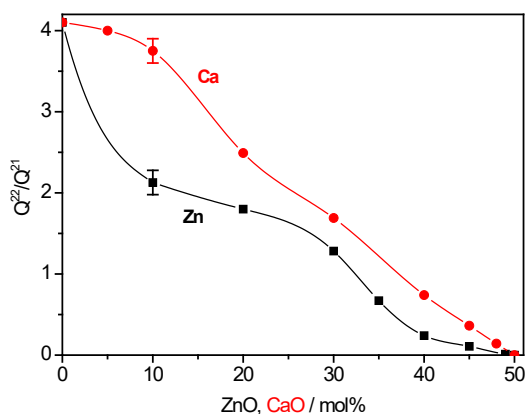


Figure 3. Compositional dependence of  $Q^{2x}$  units ratio for (a)  $x\text{ZnO}-(50-x)\text{CuO}-50\text{P}_2\text{O}_5$  and (b)  $y\text{CaO}-(50-y)\text{CuO}-50\text{P}_2\text{O}_5$  glass systems.

metaphosphate prevail in proportion  $Q^{22}/Q^{21} = 4:1$ , as followed from Figure 3. The graph also shows that zinc ions generate a higher occurrence of the ordered  $Q^{21}$  phase.

#### Density, molar volume

Density,  $\rho$ , and molar volume,  $V_m$ , provides information on the change in the compactness of the glass structure in connection with structural changes caused by the exchange of  $\text{Cu}^{2+}$  for  $\text{Zn}^{2+}$  or  $\text{Ca}^{2+}$ . The compositional dependence of the density and subsequently calculated molar volume is shown in Figure 4. The density of the glasses decreases practically monotonically in both glass lines, while  $V_m$  increases as expected.

In the case of zinc-copper glasses, the relative molecular weight of the starting copper metaphosphate ( $\text{Mr}(\text{Cu}(\text{PO}_3)_2) = 221.49$ ) is comparable to the relative molecular weight of zinc metaphosphate ( $\text{Mr}(\text{Zn}(\text{PO}_3)_2) = 223.33$ ). Thus, the decrease in density is given by the change in relative molecular weight. In our previous work

[36], it was found that both  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  cations are four-fold coordinated. The decrease in density can therefore be explained by the different spatial arrangement around the zinc and copper. Zinc with  $\text{CN} = 4$  forms tetrahedral structural units [26], while the coordination polyhedron of copper is close to square at the same  $\text{CN} = 4$  [36]. Three-dimensional tetrahedral units are more demanding in terms of volume than a two-dimensional square.

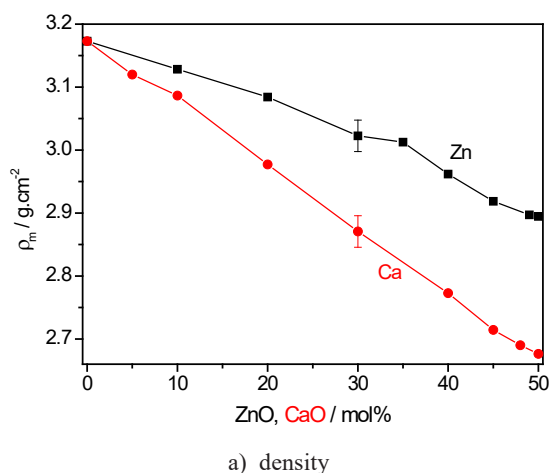
In the case of calcium-copper glasses, the course of the density can be explained by both the molecular weight of calcium phosphate ( $\text{Mr}(\text{Ca}(\text{PO}_3)_2) = 198.02$ ) in addition to the coordination number of  $\text{Ca}^{2+}$ ,  $\text{CN} = 6$  [36]. Thus, structural units of a shape close to octahedral are formed causing an even greater increase in volume compared with the square structures of copper. The densities of all three binary glasses, which diminish in the line  $\rho(\text{Cu}(\text{PO}_3)_2) > \rho(\text{Zn}(\text{PO}_3)_2) > \rho(\text{Ca}(\text{PO}_3)_2)$ , correspond well to these conclusions.

In both cases, however, the course of the concentration dependence of density and molar volume is not completely monotonic, which is rather unusual in the case of continuous exchange of divalent cations. Clear changes can be seen here at  $\sim 10$  mol. %  $\text{CaO}$  and  $35$  mol. %  $\text{ZnO}$ , see Figure 4. With some caution, it can be assumed that this course could be related to the changing ratio of metaphosphate phases  $Q^{22}/Q^{21}$ , see Figure 3.

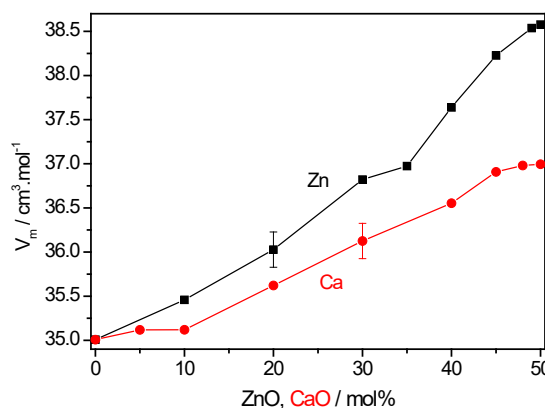
#### Thermomechanical analysis (TMA)

Two basic characteristics of glasses, the dilatometric glass transition temperature and coefficient of thermal expansion,  $\alpha$ , were determined, see Figure 5.

The coefficient of the thermal expansion is related to the vibrational amplitude of the chemical bonds, i.e. the binding energy or depth of the Morse potential, as well as its asymmetry, which is mainly related to short-range order geometry. Different asymmetries and different depths of the Morse potential correspond to



a) density



a) molar volume

Figure 4. The compositional dependence of  $x\text{ZnO}-(50-x)\text{CuO}-50\text{P}_2\text{O}_5$  and  $y\text{CaO}-(50-y)\text{CuO}-50\text{P}_2\text{O}_5$ .

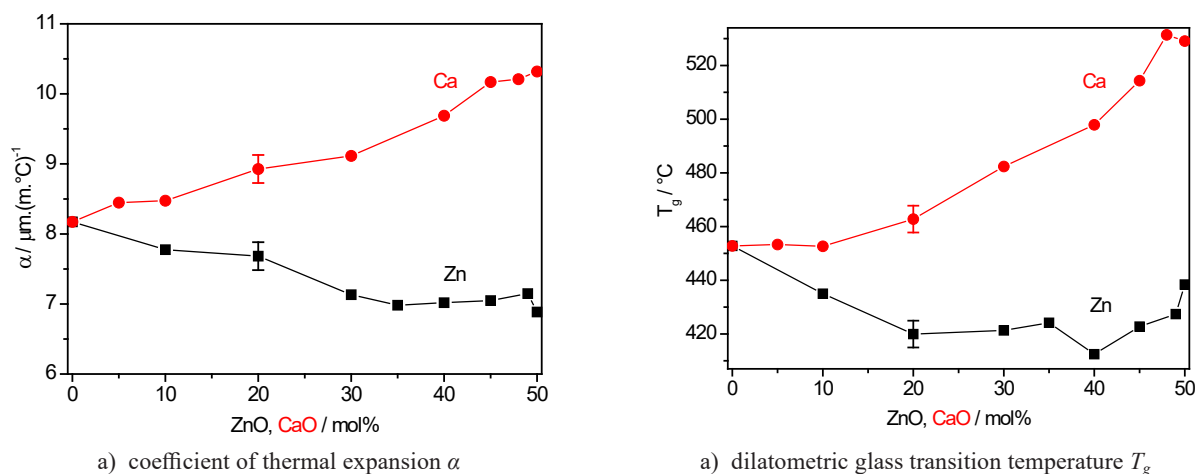


Figure 5. Compositional dependencies of the coefficient of thermal expansion,  $\alpha$ , and dilatometric glass transition temperature,  $T_g$ , for both studied glass lines.

different chemical bonds in the glass structure and the experimental value of  $\alpha$  can be seen as the mean value of these contributions, see also [39].

In the  $x\text{ZnO}-(50-x)\text{CuO}-50\text{P}_2\text{O}_5$  glasses, Figure 5a, a decrease of the coefficient of thermal expansion can be seen with the increasing content of zinc, from  $\alpha(50\text{CuO}-50\text{P}_2\text{O}_5) = 8.17 \mu\text{m}\cdot(\text{m}\cdot^\circ\text{C})^{-1}$  to  $\alpha(50\text{ZnO}-50\text{P}_2\text{O}_5) = 6.9 \mu\text{m}\cdot(\text{m}\cdot^\circ\text{C})^{-1}$ . Conversely, in the case of the  $y\text{CaO}-(50-y)\text{CuO}-50\text{P}_2\text{O}_5$  glasses, Figure 5a, the coefficient of the thermal expansion rises with increasing content of calcium, from  $\alpha(50\text{CuO}-50\text{P}_2\text{O}_5) = 8.17 \mu\text{m}\cdot(\text{m}\cdot^\circ\text{C})^{-1}$  to  $\alpha(50\text{CaO}-50\text{P}_2\text{O}_5) = 10.32 \mu\text{m}\cdot(\text{m}\cdot^\circ\text{C})^{-1}$ . Since the weaker bonds oscillate with larger amplitude, the decrease of the coefficient of thermal expansion will most likely be related to the energy of the metal-oxygen bonds present. It was found that the bond strength in the phosphate glasses decreases in the order  $\text{Zn-O} > \text{Cu-O} > \text{Ca-O}$  [36], which clearly explains both the decrease in  $\alpha$  in the case of replacing copper with zinc, and conversely its increase in the case of replacing copper with calcium.

Apart from bond energies, the changing coordination geometry of copper and calcium can also affect the increasing coefficient of thermal expansion. Larger hexacoordinated calcium structures may also contribute to the increasing thermal expansion.

At the same time as the coefficient of thermal expansion, the dilatometric temperature of the glass transition was also determined being the next important characteristic of glass. The glass transition can be seen as a steep change in the mobility of glass-forming structures (clusters) related to their different morphology and size. The relatively common, but high correlation of  $T_g$  with the energy of metal-oxygen covalent bonds, was commented on in [36]. While the energy of covalent bonds is of the order of eV, the thermal energy corresponding to the temperatures of the glass transition is up to two orders of magnitude smaller and is close to the energy of weak interactions. Thus, it is more realistic to imagine that  $T_g$

will depend on the density of weak interactions among clusters [40].

The composition dependence of the dilatometric glass transition temperature is shown in Figure 5b, confirming the results obtained from StepScan DSC [36]. Copper and zinc metaphosphates ( $\text{CN}(\text{Cu,Zn}) = 4$ ) have almost the same glass transition temperature, in contrast to calcium metaphosphate, whose glass transition temperature is significantly higher. Unlike Zn and Cu, calcium is six-coordinated, so there is greater interlinking and strengthening of the glass structure, which is reflected in the higher  $T_g$  value.

The course, however, of the composition dependencies of  $T_g$  is also non monotonic, one can see two local minima, Figure 5b. It is important to bear in mind the existence of two metaphosphate phases  $\text{Q}^{21}$  and  $\text{Q}^{22}$  with different degrees of structural disorder, which is manifested by a different mobility of the structural clusters, with this being reflected in the compositional dependence of  $T_g$ .

### Solubility

Copper-containing phosphate glasses are also currently being studied for possible use as bioglasses. From this point of view, it is important to study the effect of zinc, resp. calcium on their solubility in water, used as a polar solvent. The solubility reflects the strength and disorder of the glass structure.

When analyzing dissolution experiments, it is of essence to realize that glass, just like any solid, has a surface as an interface between two different phases (gas or liquid and solid phases) and represents a major structural disorder in the arrangement of the glass network. The closer to the surface, the more disorder in the valence angles and bond lengths will occur as well as so-called wrong bonds, i.e. bonds arising as a result of a lack of suitable bonding partners. Therefore, the

higher energy of such a glass network can be expected here, which will be more susceptible to disruption and manifest itself in faster etching of this inhomogeneous surface layer. It is therefore clear that with increasing distance from the surface into a volume of glass, i.e. with depth, the concentration of disorder decreases and finally the structure of the glass network passes into an equilibrium state with an achievable Gibbs energy minimum. Of course, the chemical composition has a decisive influence on the depth, e.g. the thickness of the surface layer. It is clear that for such a study the surface of the glass must not be chemically or mechanically modified, the measurement takes place on the virgin surface formed during the synthesis.

Beneath this surface layer, it is interesting to determine the effect of the chemical composition on the solubility of bulk glass. Since these are metaphosphate glasses, i.e. the basic structure of the glass-forming phosphate network is the same everywhere, it can be expected that the solubility will be primarily influenced by the individual metal cations and their ratio.

The dissolution results, expressed in the form of the time dependence of weight loss per unit area of both series, are shown in Figure 6 a, b. First, it is important to draw attention to the y-axes of both time dependencies of solubility. It can be seen that the solubility of glasses with zinc is about two orders of magnitude higher compared to the solubility of glasses with calcium. The weight loss of Ca-Cu-glasses with excess of Cu was close to the weighing experimental error, therefore the measurement was terminated after 30 days.

As is clear from Figure 6a, the binary copper metaphosphate glass is almost insoluble. It was found that the mass loss of  $\text{Cu}(\text{PO}_3)_2(50\text{CuO}-50\text{P}_2\text{O}_5)$  glass was close to 0.5 % after 120 days, which is within the range of measurement error, while the solubility of copper-free glass, i.e. zinc metaphosphate,  $\text{Zn}(\text{PO}_3)_2$ , is three orders of magnitude higher. Therefore, the solubility rapidly increases with the zinc content. In the case of the second glass system, CaO-CuO- $\text{P}_2\text{O}_5$ , Figure 6b, it is evident, that

with increasing concentration of calcium, the solubility also increases in the entire compositional range, but more slowly than in the case of zinc. The solubility of calcium metaphosphate,  $\text{Ca}(\text{PO}_3)_2$ , is only one order of magnitude higher compared to copper metaphosphate,  $\text{Cu}(\text{PO}_3)_2$ . These differences in solubility correlate well with the found relative ionicity of the metal-oxygen bonds in phosphates, as discussed above. It is therefore evident that compared to zinc calcium strengthens the glass structure much more and this effect is very similar to that of copper. The introduction of zinc into the glass structure brings a higher ionicity and therefore it can be assumed that these glasses will be more soluble in water than glasses with calcium. The significant decrease in the solubility of calcium glasses in a polar solvent indicates that calcium is incorporated into the glass network not as a  $\text{Ca}^{2+}$  ion, but as six-coordinated, with predominantly covalent bonds.

Based on the fact that regularly arranged structures (mainly crystals) are easily attacked by solvent, it should be possible to correlate chemical resistance to water with the ratio of more  $\text{Q}^{22}/\text{Q}^{21}$  structures. The binary copper-metaphosphate glass was found to be dominated by less ordered structural units of  $\text{Q}^{22}$ , which can be assumed to be more resistant to dissolution. With increasing  $\text{Zn}^{2+}$  and  $\text{Ca}^{2+}$  concentration, the concentration of ordered  $\text{Q}^{21}$  metaphosphate structures, which dissolve more easily, increased.

An unexpected finding is that the dissolution curves of both glass systems show changes in the slope indicating the changes in the solubility in the bulk of the glass as a function of distance from the virgin surface. This confirms our previous finding that different phases occurred in the studied glasses [36]. There are consequently in all probability segregate glass phases with a different chemical composition. However, this phase segregation was not reflected either in the  $T_g$  nor  $\alpha$ . For all the glasses only one value of the given quantity was found, which means that the chemical composition of the segregate phases does not differ all that significantly.

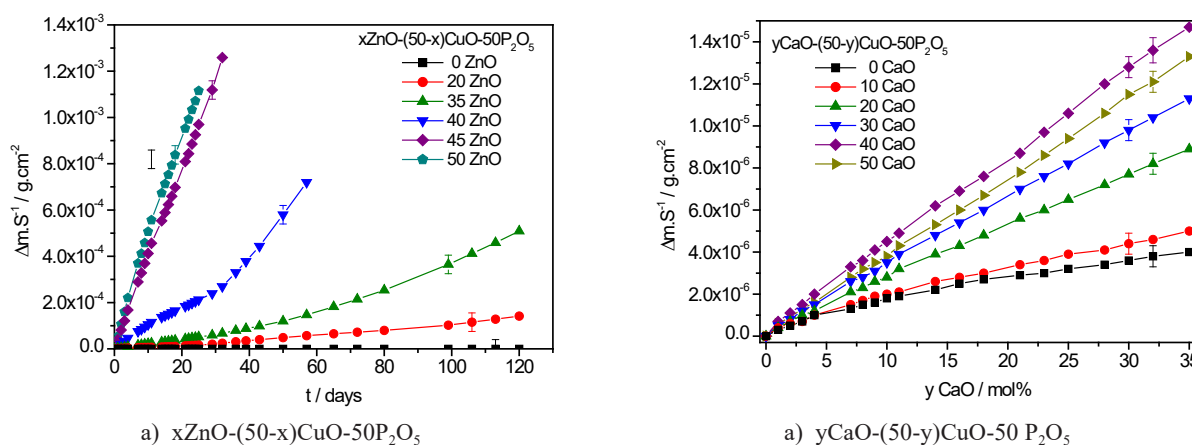


Figure 6. Time dependence of the mass change per unit area of the glass series.

In this case, these are averaged values over all phases, while solubility measurements offer a finer-scale view.

This can be seen clearly in Figure 6a, where, in particular, on the solubility curve of the 40ZnO-10CuO-50P<sub>2</sub>O<sub>5</sub> glass, the change in the slope is very clearly visible indicating, next to the existence of the surface layer, two segregated subsurface phases, which differ from each other in water solubility and thus also in the chemical composition. It is possible to conclude that the first subsurface phase dissolves more slowly than the second one. It is therefore possible to conclude that the first subsurface phase has a higher copper content, compared to the second one.

Some changes in slope are also visible in the dependencies of calcium copper phosphate glasses, but less clearly, in comparison with zinc glasses, Figure 6b. As was stated before, the solubility of glassy calcium metaphosphate is two orders of magnitude lower than that of zinc metaphosphate and thus approaches that of copper metaphosphate. Therefore, possible changes in the solubility of individual phases, differing in copper and calcium content, are less noticeable.

Using the procedure described in the experimental section, the surface layer thickness was also determined for each glass composition, as an example see Figure 7a, b. In the case of glass with 40 mol. % ZnO, the thickness of the surface layer was found to be ~115 μm, for glass with the same CaO content only ~2.5 μm. In general, the surface layer of zinc glasses is about two orders of magnitude thicker than in the case of calcium glasses, thus, the structural disorder is projected to a much greater glass volume depth, which again correlates well with the higher solubility of zinc glasses.

The compositional dependencies of the surface layer thickness in the logarithmic scale are shown in Figure 8.

It has been found that, with increasing content of zinc, the thickness of the surface layer increases significantly unlike calcium glasses. The surface layer thickness was determined for all three border binary

glasses, e.g.  $d_{\text{ZnO-P}_2\text{O}_5} = 296 \mu\text{m}$ ,  $d_{\text{CaO-P}_2\text{O}_5} = 1.8 \mu\text{m}$ ,  $d_{\text{CuO-P}_2\text{O}_5} = 0.8 \mu\text{m}$ . The solubility of these glasses decreased dramatically with decreasing thickness of the surface layer, which indicates the essential role of the metallic component of the glasses. It is therefore clear that the decreasing thickness of the surface layer and the simultaneous decreasing solubility indicate a significant strengthening of the glass network in the series  $\text{Zn} \ll \text{Ca} < \text{Cu}$ . From a chemical point of view, we can assume that the polarity of the metal-phosphate oxygen bonds plays a significant role. This correlates with the ionicity of the bonds mentioned above, Figure 2. In addition to the clear influence of metals, however, the influence of the content of ordered structures Q<sup>21</sup>, which contribute to a higher solubility of glasses, cannot be ignored. Their content is higher in glasses with zinc content, Figure 3.

With an acceptable degree of probability, we can assume that the prepared glasses are phase segregated and the presence of copper ions causes extreme reduction of water solubility in both glass series. The segregate

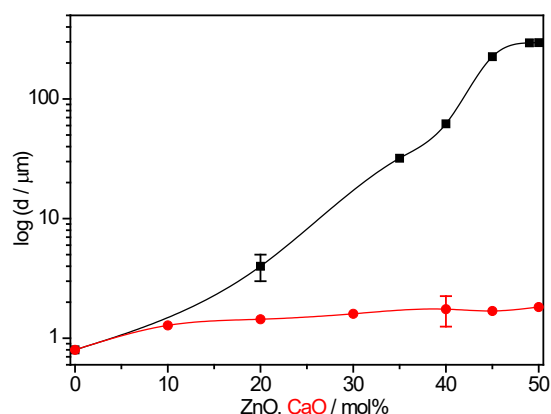
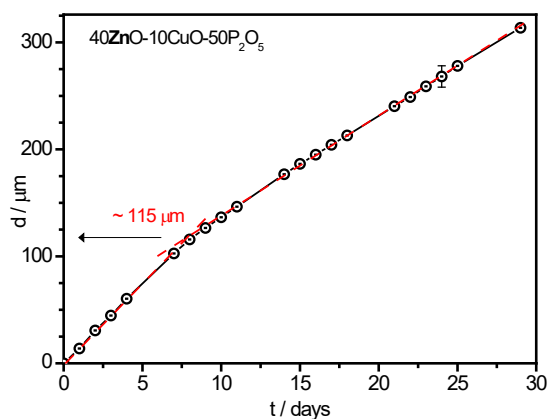
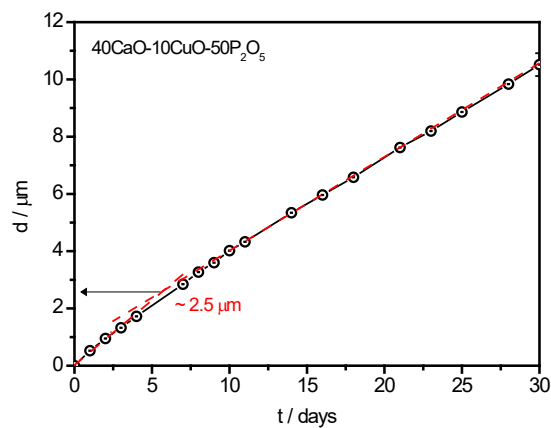


Figure 9. The compositional dependence of surface layer thickness.



a) 40ZnO-10CuO-50P<sub>2</sub>O<sub>5</sub>



a) 40CaO-10CuO-50 P<sub>2</sub>O<sub>5</sub>

Figure 7. Time dependence of the etched thickness of surface of the glass series.



phases are not made up only copper or zinc, resp. calcium ions but one of the phases is chemically richer in copper and the other phases are chemically richer in zinc, resp. calcium ions. The difference in chemical composition between the phases is so slight, however, that it could not be detected by classical methods.

### CONCLUSIONS

This work is a continuation of the study of metaphosphate glasses of the ZnO/CaO-CuO-P<sub>2</sub>O<sub>5</sub> system. Based on an extended study of Raman spectra, the ionicity of the Me-O-P bond (Me = Zn, Ca, and Cu) was assessed. The Zn-O(-P) bond was found to be the most ionic, while the Ca-O(-P) bond is relatively covalent.

The effect of increasing concentration of zinc and calcium on selected physicochemical properties of glassy copper metaphosphate was studied and the experimentally obtained results were discussed in detail from the point of view of ionicity and the structure of glasses.

Compared to copper, it was found that both zinc and calcium reduce the compactness of the glass structure, of course to a different extent, and thus affect the coefficient of thermal expansion as well as the glass transition temperature. Both these metals also increase the solubility of glasses, with calcium far less significantly than zinc. This correlates well with the found higher covalence of the bond of calcium with the oxygen of the phosphate chains and further with the higher coordination number of calcium.

Using the solubility results, the thicknesses of the surface layer of the glasses of both series were determined. A comparison of the results for binary metaphosphate glasses showed that the surface layer of copper metaphosphate is the thinnest, and as copper is gradually replaced by calcium, the thickness of the layer increases. Zinc has an even more pronounced effect on the thickness of the surface layer. In the glasses of both composition series, volume segregation of two phases differing in solubility was found.

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