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Effect of Composition of Precipitated Calcium-Copper Orthophosphates on Their Character

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Abstract—A group of crystalline and amorphous calcium-copper phosphates was synthesized by the exchange reaction between sodium orthophosphate and calcium and copper(II) nitrates in solutions within a wide range of reagent ratios $0 \le \text{Cu}\times100/(\text{Cu} + \text{Ca}) \le 100$. Conclusions on the effect of the $\text{Cu}\times100/(\text{Cu} + \text{Ca})$ ratio on the phase composition of the substances and on the state of chemical bonds therein were made on the basis of the results of X-ray phase analysis and IR Fourier and electronic spectroscopy.

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Calcium phosphate acid salts, like hydroxyapatite, tricalcium phosphate, and their amorphous analogs, are of interest as precursors of bioceramics with adjustable pore sizes [1–6]. Compounds of alkaline earth metals, silicates, and many other substances [7–11] may act as components efficiently influencing the porosity of ceramics obtained from phosphate precursors. Transition metal ions are of interest, as they allow fine control both of the microscopic structure and properties of ceramics. Copper is one of such examples, as its compounds impart strong antiseptic properties to materials [12–15]. We already described this element as a modifier of amorphous calcium phosphates, which substituted a small part of calcium cations in their composition [16]. In this communication we consider the nature of phosphates obtained from aqueous solutions at the simultaneous presence of calcium and copper in a wide range of $0 \le \text{Cu}\times100/(\text{Cu} + \text{Ca}) \le 100$ ratios.

The synthesized compounds are pasty products with moisture content of 80–90 wt %. In air at room temperature phosphates erode rather fast, losing the main part of bound water and turning to solids with humidity of no more than 20% and an inorganic substance as a remainder. Therefore the pastes were dried in a thin layer in air at room temperature to a constant weight. The table gives an idea of the chemical composition of the resulting substances.

Synthesized substances were studied by the methods of X-ray phase analysis, IR Fourier- and electronic spectroscopy.

The X-ray phase analysis has shown that precipitated phosphates after dehydration in air at room temperature turn to crystalline or amorphous substances depending on the atomic ratio $\text{Cu}\times100/(\text{Cu} + \text{Ca})$ in them (Fig. 1). The substance formed in the absence of copper represents hydroxyapatite, probably of non-stoichiometric composition [6]. Diffractograms of substances with compositions corresponding to the ratios $15 \le \text{Cu}\times100/(\text{Cu} + \text{Ca}) \le 67$ contain only one wide maximum, which points to amorphous character of the substances. Indications of the presence of another poorly formed crystal phase appear at greater copper content. The comparison of diffractograms 3 and 4 in Fig. 1 with the known published data [17] suggests that it can be a hydrated copper phosphate $\text{Cu}_3(\text{PO}_4)_2$.

The effect of composition becomes apparent in the synthesized phosphates also on the molecular level, in particular, in the state of certain chemical bonds in the substances. According to the IR spectroscopy data, P–O chemical bonds inside orthophosphate groups PO_4^{3-}, which are characteristic of hydroxyapatite, change their character in the presence of copper in samples (Fig. 2). One rather narrow peak corresponding to ν_1 and ν_3 vibrations [18, 19] is replaced by a wider band

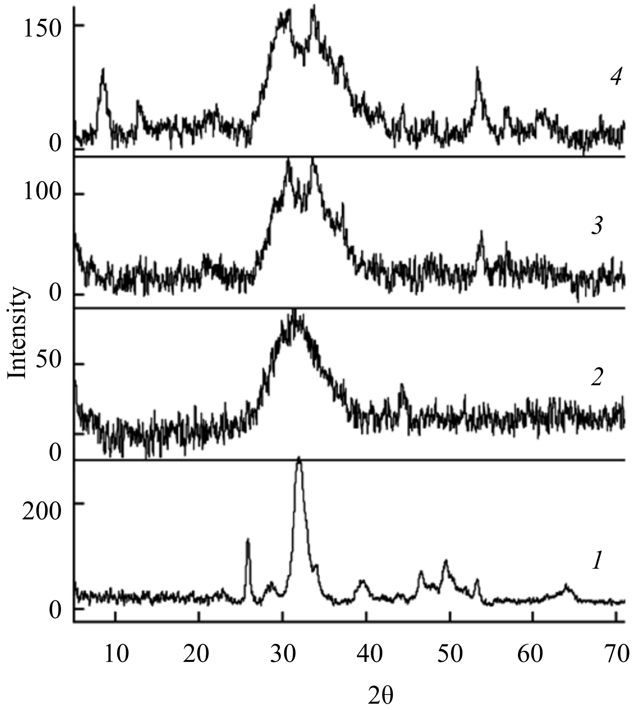

Fig. 1. Diffractograms of calcium-copper phosphates with Cu×100/(Cu + Ca) atomic ratio: (*1*) 0; (*2*) 44; (*3*) 79; (*4*) 100.

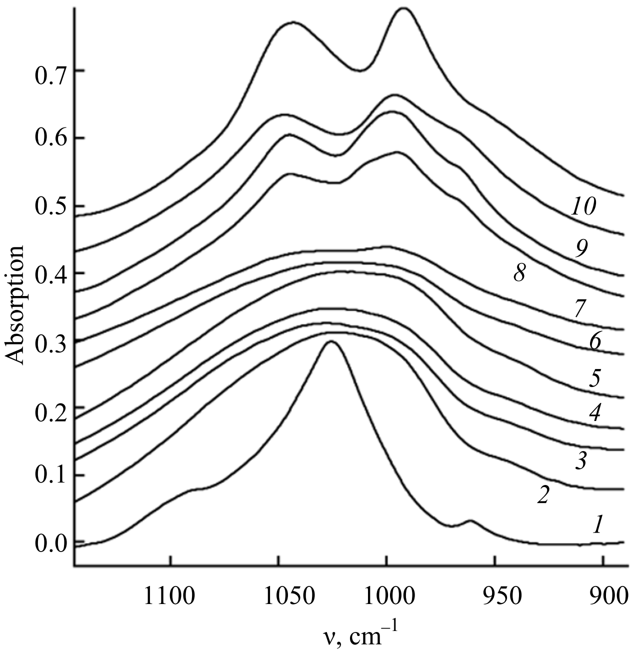

Fig. 2. IR Fourier-spectra of calcium-copper phosphates with Cu×100/(Cu + Ca) atomic ratio: (*1*) 0; (*2*) 23 ; (*3*) 26; (*4*) 44; (*5*) 61; (*6*) 67; (*7*) 74; (*8*) 79; (*9*) 93; (*10*) 100.

with a diffuse peak. This band is present in the spectra of samples 2–6, which according to X-ray phase analysis data have amorphous character. Starting from sample 7, two maxima appear on a wide absorption line, which turn to a pair of fully resolved spectral components, as the amount of copper in substances increases. The last of the samples is orthophosphate contains only copper, and maxima in its spectrum at 992 and 1042 cm^{-1} overlap each other to the least extent, therefore we can suggest that they correspond to the stretching vibrations of P–O bonds in copper phosphate. According to [20, 21], symmetric ν_s(PO) and asymmetric ν_{as}(PO) vibrations with frequencies of 930–990 and 975–1140 cm^{-1}, respectively, are actually characteristic for the IR spectra of copper orthophosphate, though similar lines correspond to analogous vibrations of basic copper phosphates and also to phosphates containing copper together with other metals, for example with zinc [22–24]. As in our case the samples are free from foreign metals, except for copper, and as hydroxy groups were not found there, the above-stated assumption seems pertinent.

Content of calcium and copper in precipitated calcium-copper orthophosphates[a]

Sample	Content, at %		Atomic ratio Cu×100/(Cu + Ca)
	Ca	Cu	
1	23.1	0.0	0
2	19.6	3.5	15
3	17.8	5.3	23
4	17.1	6.0	26
5	12.9	10.2	44
6	9.0	14.1	61
7	7.6	15.5	67
8	6.0	17.1	74
9	4.8	18.2	79
10	1.6	21.5	93
11	0.0	23.1	100

[a] Results of the analysis of precipitated phosphates after their dehydration are given.

A greater width of the absorption region in samples 2–6 points to the fact that, firstly, there is a wide scatter in energy of P–O chemical bonds and, therefore, in their length in amorphous calcium-copper phosphates. Secondly, there is no doubt that there are no dominating bonds among P–O chemical bonds. Each PO_4^{3-} anion can contain instead several P–O bonds slightly different in strength and length, and PO_4 tetrahedra themselves should be deprived of the structure, which is characteristic of them in individual crystalline phosphates, for example in hydroxyapatite or in copper orthophosphate. Obviously, in amorphous calcium-copper phosphates a great number of PO_4 groups differing in symmetry and size should exist. The most probable reason for it consists in structural perturbations, which are caused by simultaneous formation of proper environments of Ca^{2+} and Cu^{2+} ions, which consist of oxygen atoms and are different. In fact, coordination numbers of calcium with respect to oxygen in tricalcium phosphate, which is the nearest analog of hydroxyapatite, are seven and eight [25], whereas for Cu^{2+} ions in phosphates they are four and six [26]. As oxygen atoms coordinated at Ca^{2+} and Cu^{2+} ions are simultaneously bound to phosphorus atoms, PO_4^{3-} tetrahedra appear under the action of forces different in all four directions.

It should be expected that the effect of chemical composition of calcium-copper phosphates also concerns separate atoms. The presence of copper enables us to estimate it, analyzing light absorption by the substances. The absorption spectrum of a sample with the atomic ratio Cu×100/(Cu + Ca) = 23 is shown in Fig. 3a as an example. In the low-frequency region there is a wide line corresponding to *d*–*d* electron transitions in Cu^{2+} ions [27, 28, 30]. In the high-frequency part of the spectrum a narrower band with a clear maximum is observed, which corresponds to the charge transfer between oxygen atoms (2*p*) and copper ions (3*d*) [28–30]. Between these two lines in the range of about 470–490 nm there is a minimum, the position and intensity of which defines the moderately blue color of the substance.

The intensity of light reflection (scattering) by all samples, which was found from the absorption minimum, first almost linearly decreases as a copper fraction in samples increases, then, starting from the ratio Cu×100/(Cu + Ca) = 67, slightly grows, and at Cu×100/(Cu + Ca) = 79 decreases again. It seems improper to interpret such variation of the optical density for each separate section, as the intensity of substance coloring can depend not only on the state and number of light adsorption centers, but also on the microstructure, and also on the density of samples. It is possible to rely only on a common trend – the reduction of the amount of light scattered by substances with the increasing copper concentration in them. However, as judged from a parallel fully monotone decrease in the frequency of the absorption minimum (Fig. 3b), the assumption on the gradual variation in the state of Cu^{2+} electron shells is apparent.

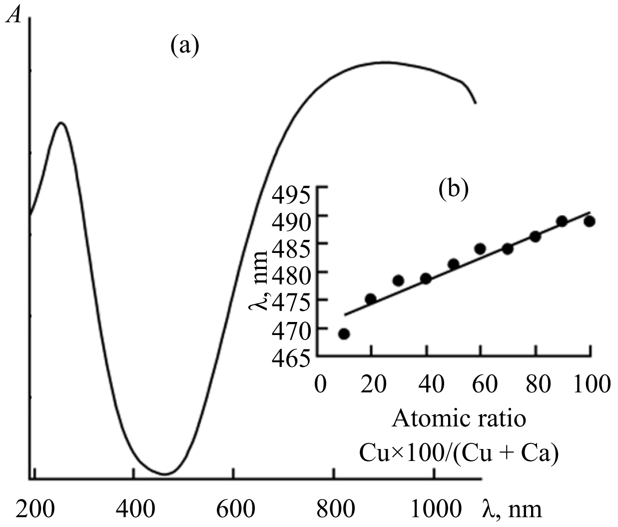

Fig. 3. (a) Example of diffuse scattering spectrum of a sample with atomic ratio Cu×100/(Cu + Ca) = 15, and (b) dependence of the light absorption minimum position on the composition of calcium-copper phosphates.

As the copper concentration in samples increases, both absorption bands in the diffuse scattering spectra weakly shift in the high-frequency region that points to a difficulty in *d*–*d* transitions and oxygen-copper charge-transfer transitions. A possible reason of it is an increase in the electronegativity of compounds owing to replacement of calcium ions in them by copper cations, the electronegativity of which is almost twice higher than that of calcium. In fact, the increase in total electronegativity in the nearest environment of each of atoms should result in the decrease in the density of negative electric charge on each separate atom (ion), and it may generate problems for interatomic electron transitions. As to the charge transfer between copper and oxygen ions, the dependence of this process on the composition can be interpreted as an evidence of the effect of composition on the state of Cu–O chemical bonds, which should be strengthened as a total amount of copper in phosphates increases.

Thus, calcium-copper orthophosphates obtained by coprecipitation from aqueous solutions and then dehydrated at room temperature in air are amorphous or poorly formed crystalline substances. At the atomic ratio Cu×100/(Cu + Ca) = 0 the crystalline calcium phosphate, non-stoichiometric hydroxyapatite, is formed, and at $67 < \text{Cu}\times100/(\text{Cu} + \text{Ca}) \leq 100$, copper orthophosphate. Products, amorphous to a various degree, correspond to intermediate compositions with ratios $15 \leq \text{Cu}\times100/(\text{Cu} + \text{Ca}) \leq 67$. The composition of substances also defines a state of P–O chemical bonds in phosphates: In amorphous substances PO_4^{3-} anions are unsystematically deformed and deprived of the symmetry characteristic of them in crystalline calcium or copper phosphates. An increase in the copper fraction in calcium-copper phosphates leads to variations in the state of Cu^{2+} cations and, possibly, of other ions, and also of Cu–O chemical bonds.

EXPERIMENTAL

The X-ray phase analysis was carried out on an X'Pert HighScore PANalytical diffractometer using CuK_α radiation at 25°C with a step of 2θ 0.0170. A layer of about 0.2 mm in width of powdery substance under study was deposited on an amorphous silicon substrate.

The IR spectra were recorded at room temperature on a ZnSe single crystal using an FT-IR Nicolet 6700 spectrometer in a distorted total internal reflection mode with a resolution of 4 cm^{-1}, accuracy of measuring ±0.5 cm^{-1}, and number of scans 32. Even coatings of about 1 mm in width of finely ground substances were deposited on a surface of a semiconducting substrate. The spectra were recorded at room temperature. Electronic spectra were taken in a diffuse scattering mode on a UV-Vis Perkin-Elmer Lambda 35 spectrometer in combination with a Lambda 2-40 solid integrating sphere. Samples for recording these spectra were formed in special molds in the form of disks of 1 cm in diameter and about 3 mm in width.

To synthesize subjects of the study, a 5% aqueous solution of sodium orthophosphate, $\text{Na}_2\text{HPO}_4\cdot12\text{H}_2\text{O}$, was treated by a solution of the same concentration containing calcium and copper nitrates in required proportions. A solution of nitrates was added dropwise with intensive stirring to a phosphate solution at room temperature. The hydrogen index of the phosphate solution was first brought to pH 9–10 by adding NaOH and was maintained at this level during the reaction. The precipitated substances were separated from a solution of salts by decantation, dispersed in distilled water with pH 8 taken approximately in the 10–20-fold excess, held for 2–3 h, and again separated from the solution. The operation was repeated up to the absence of NO_3^- ions in rinsing water. The hydrogen index of rinsing water was adjusted with an ammonia solution. The washed products were filtrated in vacuum on a "Corning" nylon filter with a pore size of 0.2 μm.

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