

SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Synthesis, Structural Features, and Color of Calcium–Yttrium Hydroxyapatite with Copper Ions in Hexagonal Channels

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Abstract—Copper-containing calcium phosphates $\text{Ca}_{5-z}\text{Y}_z(\text{PO}_4)_3\text{Cu}_x\text{OH}_{1-x-z-\delta}$, where $x = 0, 0.1, 0.3$ and $z = 0, 0.5$, with an apatite structure and a partial substitution of yttrium for calcium have been synthesized by a solid-phase method at a temperature of 1100–1150°C. The compounds have been characterized by X-ray powder diffraction and diffuse reflectance spectroscopy. It has been established that yttrium substitutes for calcium only in the Ca(2) position, and the occupancy of this position corresponds to the yttrium content $z = 0.4–0.43$. The substitution by yttrium slightly decreases the unit cell parameter of the compound (by ~0.3%) and much more considerably (by 3%) reduces the diameter of a hexagonal channel formed by Ca(2) atoms. The predominant fraction of doping copper intrudes into hexagonal channels in both unsubstituted and yttrium-substituted calcium phosphates. Unsubstituted copper-containing phosphates are pink-crimson colored, whereas their yttrium-substituted analogues have much more pale colors from nearly white to greeny beige. The absorption bands typical for a copper-containing calcium hydroxyapatite observed in diffuse reflectance spectra are strongly suppressed in yttrium-substituted samples probably due to a decreased average oxidation number of copper.

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Phosphates with an apatite structure find wide applications as sorbents, catalysts, bone tissue substitutes and, since recently, as pigments. Violet-colored copper-containing strontium hydroxyapatite was synthesized for the first time in 2002 [1]. Blue- and crimson-colored copper-containing barium and calcium hydroxyapatites were synthesized a short time later [2]. Structural characterization performed via single-crystal X-ray diffraction shows that copper atoms occupy the (0, 0, 0) positions in hexagonal channels closely to the hydrogen atom rather than the positions of the alkaline-earth metal atom in the structure of hydroxyapatite, as might be expected. This results in that copper ions turn out in linear coordination by oxygen ions [1, 2]. The samples annealed in an inert atmosphere are nearly colorless. Annealing in air or oxygen leads to the appearance of a bright color associated with a partial oxidation of copper, which initially has an oxidation number of +1. The color of similar materials does not become pale with time and is resistant to water and sunlight. For this reason, these compounds have already found application as pigments [3]. Diffuse reflectance spectra (DRSs) demonstrate the shift of the major absorption peak towards higher wavenumbers upon the passage from barium to calcium hydroxyapatite. Mixed-cation compounds

are characterized by intermediate colors, but are usually less intensely colored [4]. The hypsochromic shift of the major absorption band and the change in color from blue through violet to red may be explained by the strengthening of the crystal field that acts onto the copper cation, which is a chromophoric site. As the radius of an alkaline-earth cation decreases, the unit cell parameters of a compound and, correspondingly, the length of copper–oxygen bonds in channels decrease, thus increasing the splitting of copper ion energy levels by the crystal field [2].

It is of great interest whether further color variations are possible. The color shift to red-yellow is most important. This is due to the fact that modern yellow-red pigments are predominantly based on extremely toxic lead and cadmium compounds. At the same time, copper is less toxic: maximum concentration limit (MCL) of copper in the water of objects used for drinking and domestic-recreation purposes is nearly 1000 times higher than the MCL for cadmium and 30 times higher than the MCL for lead [5].

Relying on the above-considered trends of color variations, we may expect that a further decrease in the unit cell parameters of calcium apatite due to a partial substitution of calcium by smaller ions will favor the shift of a color shade to red-yellow. Our studies in this direction have led to the successful synthesis of calcium–lithium copper-containing apatites, whose unit

[†] Deceased.

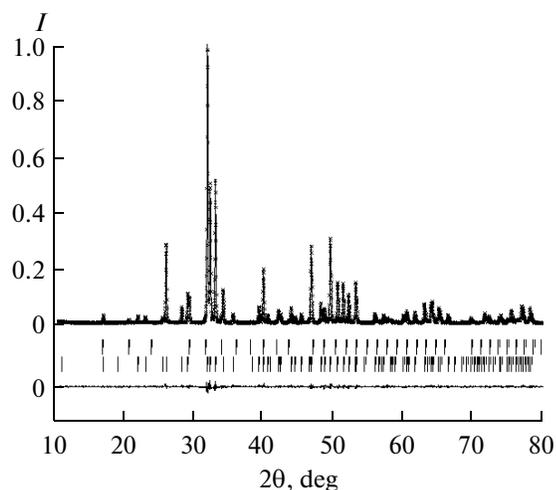


Fig. 1. Measured, calculated, and difference X-ray diffraction pattern of $\text{Ca}_{4.5}\text{Y}_{0.5}(\text{PO}_4)_3\text{Cu}_{0.3}\text{OH}_{0.2-\delta}$.

cell parameters are lower than the corresponding parameters of their calcium analogue. The color of samples varied from light pink to cherry depending on their composition and thermal treatment conditions [6]. At the same time, our attempts at substituting magnesium for calcium have led to the destruction of an apatite structure and the formation of stable tricalcium phosphate.

In this work, we report the results of our studies on the substitution of smaller yttrium ions for calcium ions in calcium hydroxyapatite with the purpose of establishing the possibility of the desired change in the color of the material.

EXPERIMENTAL

$\text{Ca}_5(\text{PO}_4)_3\text{Cu}_x\text{OH}_{1-x-\delta}$ copper-containing and copper-free (reference) hydroxyapatites and corresponding $\text{Ca}_{4.5}\text{Y}_{0.5}(\text{PO}_4)_3\text{Cu}_x\text{OH}_{0.5-x-\delta}$ hydroxyapatites, where $x = 0, 0.1, \text{ or } 0.3$, with a partial substitution of yttrium for calcium were prepared. CaCO_3 , $(\text{NH}_4)_2\text{HPO}_4$, CuO , Li_2CO_3 , and Y_2O_3 of better than chemically pure grade were used as initial reagents. The unknown index δ at the hydrogen atom takes into account the possible presence of copper ions in the oxidation state of higher than +1 and/or peroxide ions in the compound.

All necessary reagents were taken in the stoichiometric ratio per 2 g of resulting material (with a 1% deficit of phosphate). The reagents were carefully ground in an agate mortar and placed into alundum crucibles.

Thermal treatment included the following three main stages:

(1) Preliminary annealing of powders was performed without quenching at relatively low temperatures to decompose the initial carbonates and phosphates as follows: heating to 600°C for 1 h, holding for

1.5 h, heating to 800°C for 1 h, holding for 3 h, and cooling with a furnace. The resulting powders were ground in an agate mortar;

(2) Major annealing. Powders were annealed three times at 1150°C as follows: heating for 1.5 h, holding for 3 h, and cooling with a furnace. After each annealing, the samples were carefully ground in an agate mortar. The samples were then pressed into pellets and annealed with quenching at the same temperature and heating rate.

(3) Modifying annealing. The pellets were annealed at 900°C for 4 h with quenching. This schedule was used for inducing a possible modification of color in samples, because low-temperature annealing was shown to deepen the color of copper-containing hydroxyapatites [7].

The phase composition of the samples was determined by X-ray powder diffraction after each heat treatment stage using an FR-552 Guinier chamber (Ge internal standard, $\text{CuK}\alpha_1$ radiation). The X-ray diffraction patterns of the resulting samples were recorded on a Rigaku diffractometer ($\text{CuK}\alpha$ radiation; 2θ reflection angle range, $5^\circ\text{--}80^\circ$; 0.02° steps).

Crystal structure was refined into the space group $P6_3/m$ (176) by the Rietveld method using the Jana2006 software [8]. The coordinates and isotropic thermal parameters of all atoms, except for hydrogen, and the occupancy of yttrium and copper atomic positions were refined. The O(4) atom was refined in the splitted position with an occupancy of 0.5. To avoid strong correlations, the thermal parameters for Ca(2) and Y(1) and for Ca(1) and Cu(1) were taken as equal. In the presence of admixtures, the content and unit cell parameters of admixtures at fixed (by literature data) atomic positions were simultaneously refined.

DRSs were recorded on a Perkin Elmer Lambda 950 spectrophotometer within the region of 150–1170 nm using powdered samples.

RESULTS AND DISCUSSION

Phase Composition and Crystal Structure

Phase composition was monitored after each heat treatment stage. As a rule, the formation of phases was completed by the final stage of major annealing. The resulting samples represented nearly pure apatite. The yttrium-containing samples contained less than 2% of yttrium oxide as impurity. The results of the full-profile Rietveld analysis of the X-ray diffraction pattern of $\text{Ca}_{4.5}\text{Y}_{0.5}(\text{PO}_4)_3\text{Cu}_{0.3}\text{OH}_{0.2-\delta}$ are illustrated in Fig. 1.

The unit cell parameters of this compound and divergence factors are given in Table 1, and atomic coordinates and position occupancies are listed in Table 2. A crystal structure fragment is shown in Fig. 2.

As can be seen from Table 2, the introduction of copper increases the unit cell parameters. At a copper content of 0.3 mol, the unit cell volume is enlarged by 0.7%. A similar increase in volume corresponds to the

Table 1. Composition of $\text{Ca}_{5-z}\text{Y}_z(\text{PO}_4)_3\text{Cu}_x\text{OH}_{1-x-z-\delta}$ with consideration for atomic position occupancies (the nominal composition is given in brackets), their unit cell parameters a and c (space group $P6_3/m$) and unit cell volume V , divergence factors R_{wp} and RF_{all} , and the contents of minor crystalline phases in the resulting samples

Composition		$a, \text{\AA}$	$c, \text{\AA}$	$V, \text{\AA}^3$	$R_{\text{wp}}, \%$	$RF_{\text{all}}, \%$	Admixture phases, wt %
z	x						
0 [0]	0 [0]	9.4154(1)	6.8792(1)	528.13(1)	7.64	2.38	—
0 [0]	0.12 [0.1]	9.4206(1)	6.8871(1)	529.32(1)	7.16	2.33	—
0 [0]	0.28 [0.3]	9.4304(2)	6.9060(1)	531.88(2)	5.86	2.68	0.7% $\text{Ca}(\text{OH})_2$; 0.5% CaO
0.44 [0.5]	0 [0]	9.3892(2)	6.8603(2)	523.76(2)	9.01	1.88	1.7% Y_2O_3
0.42 [0.5]	0.11 [0.1]	9.3968(2)	6.8681(2)	525.21(2)	6.77	1.66	1.9% Y_2O_3
0.38 [0.5]	0.25 [0.3]	9.4094(2)	6.8844(1)	527.86(2)	4.99	1.42	2.0% Y_2O_3

earlier data [2] and indicates the intrusion of copper ions into hexagonal channels. The partial substitution of yttrium for calcium leads to a slight compression of the apatite lattice: this reduces the unit cell parameters a and c by $\sim 0.3\%$ and, correspondingly, the unit cell volume by 0.8% . When copper is introduced into yttrium-containing samples, the unit cell volume is increased almost in the same fashion as for undoped calcium apatite; that is, the effect of the introduction of yttrium and copper on the unit cell parameters proves to be additive.

The refinement of the atomic site occupancies confirms the incorporation of yttrium and copper into the lattice.

Yttrium ions occupy only Ca(2) positions. The yttrium content derived from the structure refinement is nearly 10–20% lower than its nominal level. The content of the yttrium oxide admixture in the samples amounts nearly to 0.1 mol per mole of the compound, thus giving the close-to-nominal calcium/yttrium ratio in the sum with the yttrium content in the apatite structure. Hence, the dopant yttrium is not entirely incorporated into the structure, and its small fraction remains in the admixture phase.

A decrease in the unit cell parameters upon small substitutions of yttrium for calcium in hydroxyapatite was observed in [9, 10]. According to the unit cell parameters reported in [9], the degree of reduction in the unit cell volume of hydroxyapatite may be estimated at 0.35% per yttrium molar percent. According to [10] with account for the contribution from the small substitution of the fluoride ion for the hydroxide ion, an increase in the unit cell volume may be estimated at less than 0.13% per yttrium molar percent. In both cases, the scatter of data is very wide. Our results obtained with account for the yttrium content in the structure as refined from X-ray diffraction data give $0.094 \pm 0.003\%$ per yttrium molar percent, thus being closer to the data [10].

The coordinates of most atoms are changed slightly upon the introduction of yttrium and copper and lie within three standard deviations. Considerable changes occur in the positions of Ca(2) atoms. These

atoms form hexagonal channels in the apatite structure (Fig. 2). The diameter of a channel can be determined as the double distance of the Ca(2) atom from the center of a channel (0, 0, z). The y coordinate of the Ca(2) atom will be nearly proportional to the diameter of a hexagonal channel (as the x coordinate is close to 0). The change of the Ca(2) position upon the substitution of yttrium for calcium corresponds to a nearly 3% decrease in the diameter of a channel. This is one order of magnitude greater than the relative decrease in the parameter c . Therefore, the substitution of the smaller yttrium ion for the calcium ion leads to the compression of a hexagonal channel, whereas the remaining part of the structure does not endure any appreciable change. A considerable decrease in the distance between Ca(2) atoms upon the substitution of smaller gadolinium ions for calcium ions has been reported earlier [11]. We need to note that the Ca(2) position should rather be considered as a certain averaged position: the real coordinates of calcium and yttrium ions in this position may differ from

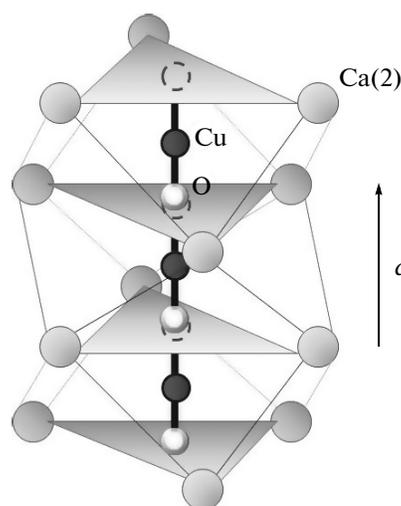


Fig. 2. Fragment of the crystal structure of calcium hydroxyapatite.

Table 2. Atomic position occupancies s , relative atomic coordinates x , y , and z , and isotropic thermal parameters U_{iso} for the crystal structure of the synthesized compounds. The compositions of the compounds are given with consideration for refined atomic positions

Atom	s	x	y	z	$U_{\text{iso}}, \text{\AA}^2$
$\text{Ca}_5(\text{PO}_4)_3\text{OH}_{1-\delta}$					
Ca1	1	1/3	2/3	0.0015(3)	0.0176(6)
Ca2	1	0.0071(2)	0.2521(1)	1/4	0.0163(5)
P1	1	0.3974(2)	0.3683(2)	1/4	0.0173(6)
O1	1	0.3269(4)	0.4826(4)	1/4	0.007(1)
O2	1	0.5852(4)	0.4646(4)	1/4	0.016(1)
O3	1	0.3375(3)	0.2540(3)	0.0714(3)	0.0232(9)
O4	0.5	0	0	0.191(1)	0.021(3)
$\text{Ca}_5(\text{PO}_4)_3\text{Cu}_{0.12}\text{OH}_{0.88-\delta}$					
Ca1	1	1/3	2/3	0.0016(3)	0.0221(6)
Ca2	1	0.0072(2)	0.2532(1)	1/4	0.0196(5)
P1	1	0.3985(2)	0.3689(2)	1/4	0.0211(7)
O1	1	0.3284(4)	0.4849(4)	1/4	0.011(1)
O2	1	0.5859(4)	0.4639(4)	1/4	0.016(1)
O3	1	0.3397(3)	0.2545(3)	0.0726(3)	0.027(1)
O4	0.5	0	0	0.214(3)	0.053(4)
Cu1	0.118(2)	0	0	0	0.0196(5)
$\text{Ca}_5(\text{PO}_4)_3\text{Cu}_{0.28}\text{OH}_{0.72-\delta}$					
Ca1	1	1/3	2/3	0.0031(3)	0.0204(7)
Ca2	1	0.0069(2)	0.2551(2)	1/4	0.0167(6)
P1	1	0.4004(3)	0.3703(3)	1/4	0.0182(8)
O1	1	0.3283(5)	0.4835(5)	1/4	0.012(1)
O2	1	0.5857(5)	0.4639(5)	1/4	0.011(2)
O3	1	0.3418(4)	0.2566(3)	0.0698(4)	0.024(1)
O4	0.5	0	0	0.216(3)	0.039(4)
Cu1	0.284(3)	0	0	0	0.0167(6)
$\text{Ca}_{4.56}\text{Y}_{0.44}(\text{PO}_4)_3\text{OH}_{0.56-\delta}$					
Ca1	1	1/3	2/3	0.0010(4)	0.0179(9)
Ca2	0.855(4)	0.0056(2)	0.2438(2)	1/4	0.0167(6)
Y1	0.145(4)	0.0056(2)	0.2438(2)	1/4	0.0167(6)
P1	1	0.4005(3)	0.3708(3)	1/4	0.0171(9)
O1	1	0.3287(5)	0.4848(5)	1/4	0.012(2)
O2	1	0.5883(6)	0.4654(5)	1/4	0.008(2)
O3	1	0.3417(4)	0.2566(4)	0.0702(4)	0.011(1)
O4	0.5	0	0	0.210(3)	0.021(4)
$\text{Ca}_{4.58}\text{Y}_{0.42}(\text{PO}_4)_3\text{Cu}_{0.11}\text{OH}_{0.47-\delta}$					
Ca1	1	1/3	2/3	0.0018(3)	0.0170(8)
Ca2	0.861(4)	0.0059(2)	0.2449(1)	1/4	0.0170(6)
Y1	0.139(4)	0.00588(19)	0.2449(1)	1/4	0.0170(6)
P1	1	0.4010(3)	0.3717(3)	1/4	0.0148(8)
O1	1	0.3273(4)	0.4845(4)	1/4	0.006(1)
O2	1	0.5891(5)	0.4669(5)	1/4	0.009(2)
O3	1	0.3433(3)	0.2573(3)	0.0713(4)	0.015(1)
O4	0.5	0	0	0.231(6)	0.036(4)
Cu1	0.105(3)	0	0	0	0.0170(8)
$\text{Ca}_{4.62}\text{Y}_{0.38}(\text{PO}_4)_3\text{Cu}_{0.25}\text{OH}_{0.37-\delta}$					
Ca1	1	1/3	2/3	0.0019(3)	0.0173(7)
Ca2	0.875(4)	0.0062(2)	0.2467(1)	1/4	0.0157(6)
Y1	0.125(4)	0.0062(2)	0.2467(1)	1/4	0.0157(6)
P1	1	0.4012(2)	0.3718(2)	1/4	0.0160(7)
O1	1	0.3289(4)	0.4853(4)	1/4	0.007(1)
O2	1	0.5896(5)	0.4683(4)	1/4	0.010(1)
O3	1	0.3449(3)	0.2591(3)	0.0702(3)	0.016(1)
O4	0.5	0	0	0.229(5)	0.034(4)
Cu1	0.253(3)	0	0	0	0.0173(7)

each other due to their different diameters and ionic charges. For this reason, the local size of a channel may vary depending on the presence or absence of yttrium ions in the nearest surrounding.

The occupancy of (0, 0, 0) positions indicates that the introduced copper almost is entirely incorporated into hexagonal channels. The introduction of copper leads to the inverse effect, namely, to an increase in the channel diameter. A similar predominant change in the channel diameter without any appreciable change in the remaining part of the structure was observed earlier for alkaline-earth and lanthanum silicates with an apatite structure upon the introduction of copper atoms into hexagonal channels [12].

We should also note some changes in the z coordinate of the O(4) atom, which is positioned in the center of a hexagonal channel. As the content of copper grows, the z coordinate systematically increases, since the position of this oxygen atom corresponds to the position of the hydroxide group in a copper-free sample [13] and represents the superposition of the oxygen atoms, one of which belongs to the hydroxide group and the other is coordinated to the copper atom, in copper-containing samples [2]. An increase in the z coordinate of the O(4) atom is also observed upon the substitution of yttrium for calcium. The average charge of anions in channels may be expected to change upon heterovalent substitutions of cations without the appearance of vacancies, so it is most probable that the O(4) atom in an yttrium-substituted compound represents the superposition of the hydroxide oxygen atom and the O^{2-} anion. The doubly charged oxygen anions in the apatite structure generally occupy the position close to (0, 0, 0.25) [14], thus leading to the corresponding shift of the O(4) averaged position.

Diffuse Reflectance Spectroscopy

Copper-containing calcium hydroxyapatites are pink ($x = 0.1$) and crimson ($x = 0.3$). Yttrium-substituted copper-containing samples are very slightly colored. The sample with the lower copper content is nearly white, and the sample with the highest copper content is greeny beige.

The DRSs of copper-containing samples are shown in Fig. 3. The spectra of the reference samples contain the following three absorption bands: the major strong band at 537–542 nm, a medium-strength absorption band (shoulder) at 440–450 nm, and a weak absorption band at 700–760 nm. These bands are in a good agreement with the literature data [2]. The intensity of absorption grows proportionally to an increase in the content of copper.

The addition of yttrium strongly suppresses the major band and considerably decreases the overall absorption intensity. Weak absorptions below 450 nm and above 700 nm persist. These changes are in a good agreement with the observed very pale greeny beige

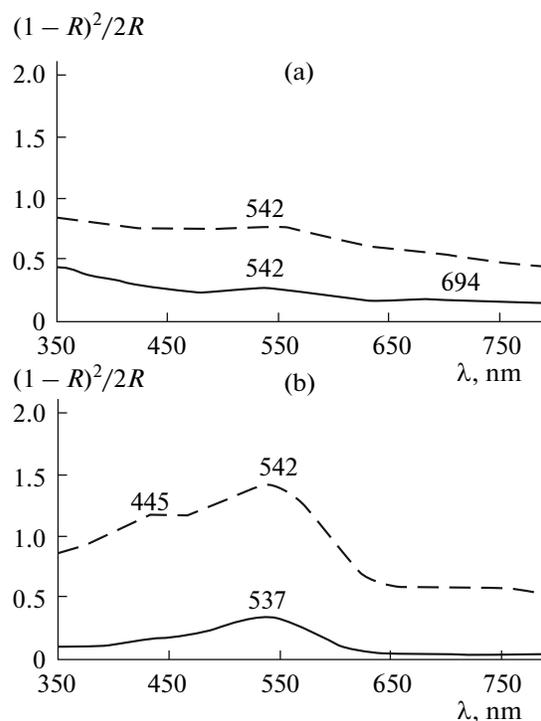


Fig. 3. DRSs of copper-containing samples (Kubelka–Munk function) for the nominal compositions (a) $Ca_{4.5}Y_{0.5}(PO_4)_3Cu_xOH_{1-x-\delta}$ and (b) $Ca_5(PO_4)_3Cu_xOH_{1-x-\delta}$ at $x = 0.1$ (solid line) and $x = 0.3$ (dashed line).

shade of the yttrium-containing samples. The weakening of the major bands may be due to that the heterovalent substitution of more highly charged yttrium for calcium may stabilize the copper oxidation state of +1 in such a fashion that the fraction of copper with an increased oxidation state that causes the typical absorption and color of a compound is reduced. At the same time, the greeny shade produced by weak absorption at the edges of the visible spectrum may indicate the presence of small amounts of copper that has an oxidation state of +2 and is incorporated in either undetected admixture phases or other positions of the apatite lattice. The latter is more probable and agrees with the conclusions [7] derived from the analysis of the spectra of a series of copper-containing calcium apatites as regards a possible intrusion of small amounts of copper into calcium positions.

In summary, copper-containing calcium phosphates with a hydroxyapatite structure and a partial cationic substitution of yttrium for calcium have been synthesized. Their crystal structures have been refined, and their DRSs have been studied. Yttrium ions have been established to substitute for Ca^{2+} ions in the Ca(2) position, thus leading to a considerable decrease in the diameter of a hexagonal channel and a slight decrease in unit cell parameters. The major fraction of the introduced copper is incorporated into hexagonal channels of both unsubstituted and yttrium-

substituted calcium phosphates. The addition of yttrium ions does not lead to any appreciable shift of the major band in the visible region (537–542 nm) of absorption spectra, although the intensity of the major bands decreases manifold and the typical pink-crimson color of samples nearly disappears.

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