



Synthesis and characterization of the Bi-for-Ca substituted copper-based apatite pigments



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ABSTRACT

Substitution of Bi for Ca in the red-violet pigment $\text{Ca}_{10}(\text{PO}_4)_6\text{Cu}_y\text{O}_2\text{H}_{2-y-\delta}$ has been studied in order to access possibilities to vary the color of the pigment. Synthesized compounds have been investigated by powder X-ray diffraction, diffuse reflectance (ultraviolet-visible-near infrared range) and Raman spectroscopy. Initial Bi-free samples contain Cu in the hexagonal channels, and a fraction of the Cu atoms constitutes recently discovered chromophore $[\text{O}-\text{Cu}^{\text{III}}-\text{O}]^-$ -units. Bi^{3+} occupies Ca^{2+} position in the hexagonal channel walls and causes the reduction of the chromophore concentration. A small fraction of Cu^{2+} substitutes Ca^{2+} and forms a new chromophore characterized by the main absorption band at 400 nm and the resonant Raman band at 593 cm^{-1} . Consequently, Bi-doping suppresses the initial red-violet color of the pigment while a yellow tint emerges. This may open an opportunity to develop new less-toxic yellow pigments.

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1. Introduction

In spite of the well-established manufacturing of inorganic pigments with a huge diversity in color there is a need to make the pigments more environmentally friendly and substitute some toxic or expensive pigments especially in the yellow-orange-red color range [1].

A new prospective pigment series developed recently represents alkaline-earth-metal phosphates $\text{M}_{10}(\text{PO}_4)_6(\text{Cu}_x\text{O}_2\text{H}_{2-x-\delta})$ with an apatite structure containing Cu-ions in the hexagonal channels [2–9]. The first brightly colored blue-violet copper-doped strontium hydroxyapatite was synthesized in 2002 [3]. Further investigations showed that copper doping made the barium hydroxyapatite blue and the calcium hydroxyapatite red-violet [4–6]. In these compounds, Cu-atoms formally substitute hydrogen of the $[\text{OH}]^-$ groups and are located at the (0,0,0) position. Such an arrangement provides linear coordination of Cu by two oxygen atoms (Fig. 1). The atomic group containing Cu^+ is described as a monomer $[\text{O}-\text{Cu}-\text{O}]^{3-}$ -ion or an oligomer $[\text{O}-\text{Cu}_n-\text{O}_{n+1}]^{(n+2)-}$

inside the hexagonal channel of the apatite-type structure [3–8]. The color arises on partial oxidation of Cu^+ in the channel. Quite recently it has been established that copper in such compounds behaves a non-trivial way: it exists in two oxidation states, +1 and +3; and the color is produced by a new chromophore moiety, linear $[\text{O}-\text{Cu}^{\text{III}}-\text{O}]^-$ -ion, confined in the channel [7]. It is characterized by the main absorption band at 595, 565, and 537 nm in the diffuse reflectance spectra of the Ba, Sr, and Ca-apatite respectively [3–5]. Hence the decrease of cation size and increase of a site-field effect (cation field strength) provides a regular blue-shift of the band. One may consider that a smaller cation or a cation with higher charge would further shift the band so that red-violet color of Ca-apatite would move to red-orange-yellow range.

Recently we have reported the results of Y- and Li-doping of the Ca-apatite pigment [8,9]. The introduction of Y causes almost total disappearance of the initial color. Y^{3+} substitutes Ca^{2+} only in position M(2), these cations form the walls of the hexagonal channels (Fig. 1) [9]. The increased positive charge of the walls is assumed to destabilize higher oxidation state of intrachannel copper ions, which makes the formation of the chromophore $[\text{O}-\text{Cu}^{\text{III}}-\text{O}]^-$ improbable. In contrast to that the Li-doping maintains the intense color with its certain change to a deeper wine-red tint, probably due to the low positive charge of Li-ion [8].

Obviously further research on the chemical modification of the pigment is required to find the ways to vary its brightness and tint. In the current paper we consider results of the Bi-doping of such

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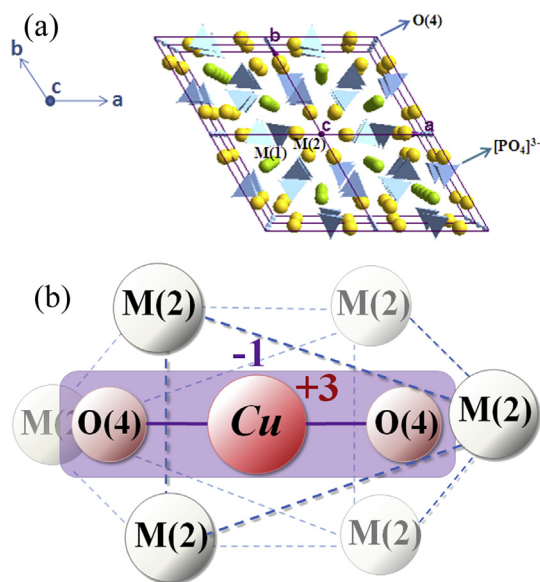


Fig. 1. Scheme of the apatite-type crystal structure (a.) and linear $[O-Cu^{III}-O]^-$ anion inside the hexagonal channel of the copper-doped hydroxyapatite (b.). M(1) represents the position of metal cations, which are surrounded by oxygen ions of the PO4 groups. M(2) represents the position of metal cations, which form the hexagonal channel's walls. Bismuth ions occupy only the M(2) position.

Ca-apatite pigments. In comparison with Y^{3+} , the cation Bi^{3+} has a bigger size (slightly exceeding that of Ca^{2+}) and forms the metal-oxygen bonds with higher covalent character. Therefore Bi^{3+} represent an interesting alternative dopant which may influence differently on the properties of the apatite pigments, at the same time providing high cation field strength required to keep the absorption band in the high-frequency region.

2. Experimental

Three types of the compounds based on calcium hydroxyapatite were prepared: bismuth-doped (Bi-for-Ca substituted), copper-doped (Cu-for-H substituted), bismuth-and-copper-doped, with general nominal composition $Ca_{10-x}Bi_x(PO_4)_6O_2H_{2-x-y}Cu_y$, where $x_0 = 0, 0.5, 1, 2$ and $y_0 = 0, 0.2, 0.6$, further abbreviated as **Bx₀C10y₀**. In addition, a cation-deficient sample $Ca_9Bi_{0.8}Cu_{0.2}(PO_4)_6O_2H_{1.4-\delta}$ was prepared and designated as **B0.8C2**. $CaCO_3$, $(NH_4)_2HPO_4$, Bi_2O_3 and CuO were mixed in appropriate stoichiometric amounts. A small excess of $CaCO_3$ ($\approx 4\%$) was added to bismuth-free samples to suppress the formation of $Ca_3(PO_4)_2$. Samples were ground in an agate mortar and solid state synthesis was carried out according to the following scheme:

1. Heating in the muffle furnace for 2 h to 600 °C, holding for 1 h, then heating for 1 h to 800 °C, holding for 2 h. Cooling in the switched off furnace.
2. Heating for 1.5 h to 1000 °C (or 1150 °C for **B0C10y₀** series), holding for 5 h. Air quenching. This procedure was repeated 4 times.
3. Inserting into the preheated to 1000 °C (to 1150 °C for **B0C10y₀** series) muffle furnace and holding for 2 h. Air-quenching by pouring the powders on the aluminum foil cooled on ice.

Samples were ground in an agate mortar after each annealing. The air-quenching saves the color in contrast to free cooling in the switched-off furnace.

All powder XRD patterns were registered using a RIGAKU diffractometer (CuK_α radiation; angle range $2\theta = 5-80^\circ$;

step = 0.02°). Crystal structures of the synthesized materials were refined by the Rietveld method in space group $P6_3/m$ using the JANA 2006 software. Refined parameters were the following: unit cell dimensions, atomic positions (except hydrogen; O(4) was refined at the (0,0,z) split position) and thermal displacement factors, calcium–bismuth and copper occupancies at M(2) and (0,0,0) positions correspondingly. Using the occupancies, experimental x and y values were obtained for the composition $Ca_{10-x}Bi_x(PO_4)_6O_2H_{2-x-y}Cu_y$. Raman spectra were registered on a RENISHAW in Via Reflex (scanning range = 100–1500 cm^{-1} , $\lambda = 514$ nm). Diffuse reflection spectra were recorded on a Perkin Elmer Lambda 950 spectrometer (integrating sphere with SPECTRALON top-coating; the scanning step = 1 nm; output data was recalculated using Kubelka-Munk function; scanning range: from 350 to 1000 nm). Colorimetric measurements in CIE $L^*a^*b^*$ color space were provided using X-Rite Eye-One Pro monitor calibrator (scanning range = 400–800 nm; step = 10 nm; standard illuminant D_{50}) and reflex camera Olympus e-420 (5400K illuminant; ISO = 200; lightroom with length-width-depth = 35 cm – 25 cm – 32 cm) and the PhotoImpact 12 software. Correlation graphs on L^* , a^* , and b^* are presented in [Appendices](#).

3. Results and discussion

3.1. Details of the crystal structure

The sample parameters under discussion are collected in [Table 1](#). Scheme of the apatite lattice is shown in [Fig. 1](#). All copper-doped samples are colored and all of the copper-free samples are white. The color of the copper-doped bismuth-free compounds is the same, as previously described for such pigments [\[4\]](#). On the bismuth-doping the color of the copper-doped samples changes to lighter and softer tints. According to XRD analysis all obtained samples represent the apatite phase ([Supplement, Fig. A1](#)). Bismuth-free samples contain the $Ca(OH)_2$ and CaO admixtures. They may arise because of the small overstoichiometry of $CaCO_3$ in the initial mixture (see Experimental) which yielded CaO on annealing and $Ca(OH)_2$ on the subsequent sample exposure to air moisture. Bismuth-doped samples with the highest Cu-content contain the CuO admixture (less than 0.5%), indicating that not all of the copper has been incorporated in the crystal cell. In some samples, unidentified reflections are observed with intensities below 2%. In any case the content of the admixture phase (and intensity of the admixture reflections) did not exceed 3%.

Here we consider unit cell parameters, diameter of the hexagonal channel d (specified as double distance between the M(2) and (0,0,0.25) position), and occupancies of specific sites by Bi and Cu.

3.1.1. Bismuth-doped samples

Earlier it has been shown that upon the calcium by bismuth substitution in hydroxyapatite, the unit cell parameters increase [\[10\]](#), as it is expected considering a little bigger radius of Bi^{3+} in comparison with Ca^{2+} (1.03 and 1.00 Å respectively for coordination number 6) [\[11\]](#). Furthermore, bismuth ions occupy only the M(2) position, and O(4) is located in the hexagonal channel at (0,0,0.25). As can be calculated from the data presented in Ref. [\[10\]](#) the distance M(2)–O(4) shrinks during the bismuth's doping. The considered distance is equal to half of the channel diameter d , therefore the latter also drops with the Bi^{3+} for Ca^{2+} substitution.

Our results confirm that on bismuth doping the cell parameters and unit cell volume V increases and d decreases ([Fig. 2](#), [Table 1](#)); Bi^{3+} is located only at the M(2) position and its refined quantity x is close to the nominal value. The dependence between V and x is practically linear with the slope 4.486 Å³/ x . The channel diameter decreases approximately linearly with the slope -0.237 Å/ x . The latter means that in spite of the bigger size of Bi^{3+} the M(2) atoms

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