



## Synthesis and characterization of the copper doped Ca-La apatites



M.A. Pogosova<sup>a,\*</sup>, I.L. Kalachev<sup>a</sup>, A.A. Eliseev<sup>a</sup>, O.V. Magdysyuk<sup>b</sup>, R.E. Dinnebie<sup>b</sup>,  
M. Jansen<sup>b</sup>, P.E. Kazin<sup>a</sup>

<sup>a</sup> Department of Chemistry, Moscow State University, 119991 Moscow, Russian Federation

<sup>b</sup> Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

### ARTICLE INFO

#### Article history:

Received 18 February 2016

Received in revised form

23 May 2016

Accepted 24 May 2016

Available online 27 May 2016

#### Keywords:

Apatite

Pigment

Copper

Color

Lanthanum

### ABSTRACT

Copper-containing Ca-La hydroxyapatites (HAPs) with chemical compositions  $\text{Ca}_{10-x}\text{La}_x(\text{PO}_4)_6\text{O}_2\text{H}_{1.5-x-y}\delta\text{Cu}_y$  ( $x = 0-1.79$ ;  $y = 0-0.57$ ) were synthesized by solid state reaction. Structural parameters and atomic positions were refined using the Rietveld method in space group  $P6_3/m$ . It was found that  $\text{La}^{3+}$  ions occupied the Ca(2) position only and copper ions were located mainly inside the hexagonal channel. In contrast to known red-violet copper-doped Ca-apatites, the copper-doped Ca-La apatites exhibited lighter colors varying from pink to pale yellow and blue-grey tints. Chromophores in the compounds were characterized by diffuse reflectance spectroscopy, colorimetry, and resonant Raman spectroscopy.

© 2016 Elsevier Ltd. All rights reserved.

### 1. Introduction

Apatite type phosphates with the general formula  $\text{M}_{10}(\text{PO}_4)_6\text{A}_2$  (M – bivalent metal (Ca, Sr, Ba, Pb etc.) or monovalent-trivalent metal's mixture; A – OH or halogen) are widely used in different areas including medicine (bone implants, remedies) [1,2] and industrially as sorbents and catalysts [3–6]. They are of interest as materials for ion conductors [7] and luminophores [8,9]. An additional application for apatite-type compounds has been found recently: copper-doped apatites happened to exhibit bright colors [10,11] and one compound has been already produced as an inorganic pigment [12].

In connection with the high production volume of inorganic pigments with a wide range of colors the development of environmentally-friendly pigments is a vexing problem. Especially for yellow-orange pigments: contemporary inorganic dyes of this color range are mainly based on toxic lead and cadmium compounds. The recently developed brightly colored copper-doped alkaline-earth apatite-type phosphates have a general formula

$\text{M}_{10}(\text{PO}_4)_6(\text{Cu}_x\text{O}_2\text{H}_{2-x-\delta})$  [10,11]. The copper ion substitutes hydrogen occupying position (0,0,0) inside the hexagonal channel and thus forming a linear monomer  $[\text{O}-\text{Cu}-\text{O}]^{3-}$  or oligomer  $[\text{O}-\text{Cu}_n-\text{O}_{n+1}]^{(n+2)-}$  anion (Fig. 1b) [10,11,13–16]. The color originates due to partial oxidation of  $\text{Cu}^+$ . Quite recently it has been shown that the color is produced by an unusual chromophore group — linear  $[\text{O}-\text{Cu}-\text{O}]^-$  anion situated in the hexagonal channel [16].

Copper-doped calcium apatite exhibits 3 absorption bands: the main intense band **A** at 537 nm, a weak band **B** around 750 nm and a shoulder **C** at 450 nm [17]. **A** and **B** have been attributed to the main chromophore formed by the oxidized intrachannel copper ions. **C** has been assigned to an additional chromophore in trace quantities. Furthermore the relationship between relative intensity of the observed bands and the content of the copper ions points to the existence of one more absorption band which overlaps with **B** but has hypsochromically shifted maximum. The authors proposed that this band was also linked to the additional chromophore.

The wavelength of the main absorption band **A** depends on the nature of the alkaline-earth metal M: 595 nm for Ba, 565 nm for Sr, and 537 nm for Ca [10,11,14]. Therefore, the rise of the cation size (and decrease of the cation field strength) leads to the regular bathochromic shift of the band. Hence, one might suggest that the use of a smaller-size cation or a cation with higher charge may change the red-violet (magenta) color of copper-doped calcium hydroxyapatite (Ca-HAP) to one in the red-orange-yellow range.

\* Corresponding author. Tel.: +7 (495) 939 34 40.

E-mail addresses: [pogosova.m.a@yandex.ru](mailto:pogosova.m.a@yandex.ru) (M.A. Pogosova), [martefyo@gmail.com](mailto:martefyo@gmail.com) (I.L. Kalachev), [eliseev@inorg.chem.msu.ru](mailto:eliseev@inorg.chem.msu.ru) (A.A. Eliseev), [oxana.magdysyuk@diamond.ac.uk](mailto:oxana.magdysyuk@diamond.ac.uk) (O.V. Magdysyuk), [r.dinnebie@fkf.mpg.de](mailto:r.dinnebie@fkf.mpg.de) (R.E. Dinnebie), [m.jansen@fkf.mpg.de](mailto:m.jansen@fkf.mpg.de) (M. Jansen), [kazin@inorg.chem.msu.ru](mailto:kazin@inorg.chem.msu.ru) (P.E. Kazin).

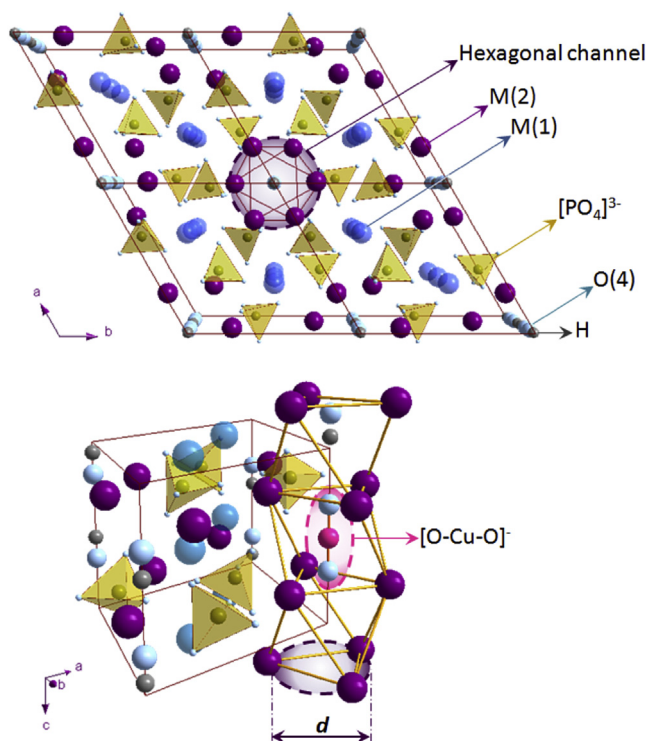


Fig. 1. Crystal structure of the hydroxyapatite (a.) and the position of the main chromophore, intrachannel linear anion  $[O-Cu-O]^-$  (b.).

However, recently reported results show that the partial substitution of Ca influences the color in another way. The substitution by trivalent cations  $Y^{3+}$  and  $Bi^{3+}$  causes the disappearance of the initial magenta color [18,19]. Both of the cations occupy only the Ca(2) position, which form the wall of the hexagonal channels (Fig. 1). Intrachannel copper ions are situated quite close to Ca(2) position (Fig. 1b). Hence, yttrium and bismuth ions may strongly influence the chromophore  $[O-Cu-O]^-$ . The substitution of Bi for Ca suppresses the chromophore by simultaneous (i) limiting the copper introduction into the channel and (ii) hindering the oxidation of colorless  $[O-Cu-O]^{3-}$  to chromophore  $[O-Cu-O]^-$  [18]. Both effects are apparently linked to more covalent nature of  $Bi^{3+}(2)-O^{2-}(4)$  bond in comparison with  $Ca^{2+}(2)-OH^-(4)$ . The electron density is shifted towards  $Bi^{3+}$  from the  $OCuO$ -group thus destabilizing the latter, especially if copper is in high oxidation state. While the initial chromophore disappears on the doping, another type of chromophore which is formed by copper ions in Ca(1)/Ca(2) positions arises [18]. This chromophore adds the yellow color component and changes the original magenta color of Cu-doped Ca-HAP to the sand-yellow color of Cu-doped Ca-Bi-HAP.

Lanthanum cation  $La^{3+}$  has the same size and charge as  $Bi^{3+}$  and may have a similar influence on the behavior of the chromophore. However, in contrast to bismuth,  $La^{3+}$  has no lone electron pair, so the  $La^{3+}(2)-O^{2-}(4)$  bond may be less covalent than  $Bi^{3+}(2)-O^{2-}(4)$  and one may consider that La-for-Ca substitution would not impede the introduction of copper ions in the channel to such extent as the Bi-for-Ca substitution does. In this paper, we describe results on synthesis and study of such copper-doped Ca-La-HAPs.

## 2. Experimental

Chemical grade  $CaCO_3$ ,  $(NH_4)_2HPO_4$ ,  $La(NO_3)_3 \cdot 6H_2O$  and CuO were used for solid state synthesis of three types of compounds: lanthanum-doped (La-for-Ca substituted), copper-doped (Cu-for-H

substituted), and lanthanum-and-copper-doped.  $La(NO_3)_3 \cdot 6H_2O$  was previously annealed at  $850^\circ C$  for 2 h and decomposed to  $La_2O_3$  which was used for the main synthesis. The general formulas of obtained compounds is  $Ca_{10-x_0}La_{x_0}(PO_4)_6O_2H_{2-x_0-y_0-\delta}Cu_{y_0}$  where  $x_0 = 0, 0.5, 1, 2$  and  $y_0 = 0, 0.2, 0.6$ . As it is known that the Cu-for-Ca substitution in Cu-doped Ca-Bi-HAP leads to a yellow chromophore formation [18], in order to increase quantity of this possible chromophore the additional samples with small cation deficiency were prepared:  $(Ca_9La)_{0.99}(PO_4)_6O_2H_{2-x-y-\delta}Cu_y$  where  $y_0 = 0, 0.2, 0.6$ . Indexes  $x_0$  and  $y_0$  represent nominal compositions. These compounds further will be denoted as **Lx<sub>0</sub>C10y<sub>0</sub>** for cation-stoichiometric and **L99C10y<sub>0</sub>** for cation-deficient series. All samples were obtained by solid state synthesis according to the next method: reagents were mixed in stoichiometric proportions in quantities to obtain ca. 2 g of the final compound and ground in an agate mortar. The obtained powders were annealed in a muffle furnace at  $600^\circ C$  (heating for 1 h, holding for 1 h) and then at  $800^\circ C$  (heating for 1 h, holding for 3 h) with subsequent grinding in an agate mortar. This step provided decomposition of calcium carbonate and ammonium hydrophosphate to calcium phosphates without the loss of phosphorus. The powders obtained after the first step were annealed twice at  $1150^\circ C$  (heating for 1.5 h, holding for 5 h, air quenching) with intermediate regrinding in an agate mortar. Then the powders were pressed into pellets and annealed at  $1150^\circ C$  (heating for 1.5 h, holding for 5 h). The annealing was carried out twice with air quenching. After the second anneal the pellets were grinded into a powder.

PXRD patterns for all target samples were registered using a Rigaku D/Max-2500 diffractometer (with  $CuK_{\alpha}$  radiation and  $2\theta$  range from  $5$  to  $80^\circ$ , step =  $0.02^\circ$ ). X-Ray diffraction was used after each step of synthesis to control the phase composition of the samples. PXRD patterns with high intensity exceeding  $10^5$  counts were additionally registered for selected samples on Bruker-AXS D8 (with  $CuK_{\alpha 1}$  radiation and  $2\theta$  range from  $10$  to  $120^\circ$ , step =  $0.01^\circ$ ). Crystal structure of obtained compounds were refined by the Rietveld method in space group  $P6_3/m$  using the JANA 2006 software [20] with refined parameters analogical to those described in Ref. [18]: unit cell dimensions; atomic positions (except hydrogen; O(4) was refined at the (0,0,z) split position) and atomic displacement parameters; calcium and lanthanum occupancies at M(2) position; copper occupancies at (0,0,0) position. Estimated values for  $x$  and  $y$  of  $Ca_{10-x}Bi_x(PO_4)_6O_2H_{2-x-y-\delta}Cu_y$  were considered using the refined occupancies. Raman spectra were registered on a RENISHAW in Via Reflex (scanning range =  $100-1500\text{ cm}^{-1}$ ,  $\lambda = 514\text{ nm}$ ). The color of the target samples was characterized using diffuse reflectance spectroscopy recorded on the Perkin Elmer Lambda 950 spectrometer (13 cm integrating sphere with SPECTRALON top-coating, scanning range: from  $200$  to  $1200\text{ nm}$ , scanning step =  $1\text{ nm}$ ). Colorimetric measurements in CIE  $L^*a^*b^*$  color space were provided using reflex camera Olympus e-420 (5400 K illuminant; ISO = 200; lightroom with length-width-depth =  $35\text{ cm}-25\text{ cm}-32\text{ cm}$ ) and the PhotoImpact 12 software [18].

## 3. Results and discussion

### 3.1. Details of the crystal structure

The hydroxyapatite crystal structure is shown in Fig. 1. Selected results of Rietveld refinement are presented in Table 1. Diffraction patterns and further crystallographic data are shown in Fig. 2 and in the Supplementary Information, Figs. A1–A12, Tables A1–A12. All the samples represent apatite as a major phase. Some samples contain admixtures: calcium and/or lanthanum phosphates with mass fraction below 12%. The unit cell parameters, nominal and

Download English Version:

<https://daneshyari.com/en/article/175375>

Download Persian Version:

<https://daneshyari.com/article/175375>

[Daneshyari.com](https://daneshyari.com)