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Crystal structure details of La- and Bi-substituted hydroxyapatites: Evidence for LaO^+ and BiO^+ with a very short metal–oxygen bond

Pavel E. Kazin [a,*], Mariam A. Pogosova [a], Lev A. Trusov [a], Irina V. Kolesnik [a], Oxana V. Magdysyuk [b], Robert E. Dinnebier [b]

[a] Department of Chemistry, Moscow State University, 119991 Moscow, Russia
[b] Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

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ABSTRACT

Crystal structures of substituted apatites with general formula $Ca_{10-x}M_x(PO_4)_6(OH_{1-\delta})_{2-x}O_x$, where M=La, Bi, $0 \le x < 2$, were refined using high-resolution X-ray powder diffraction patterns. Individual positions for Ca^{2+} and M^{3+}-ions localized near Ca2-site were determined. The M^{3+}-ion was found shifted toward the hexagonal channel center with respect to the Ca^{2+}-ion, forming very short bond with the intrachannel O^{2-}, while leaving considerably longer distances to other oxygen atoms, which suggested the existence of a MO^+ ion. Distinct bands of stretching M–O modes were observed in the Raman and FT-IR spectra of the compounds. The bond lengths for BiO^+ and LaO^+ were estimated to be 2.05 (1) and 2.09(1) Å correspondingly. The latter was almost 0.3 Å lower than the shortest La–O bond in La_2O_3. The realization of such a strong lanthanide–oxygen bond in a crystal lattice could provide a very high axial ligand field and might be implemented to develop high-energy-barrier single-molecule magnets as well as to tune properties of lanthanide-based luminophores.

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1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ adopts large diversity in the cation and anion substitution while retaining its initial structure [1]. In particular lanthanide (Ln) for Ca substitutions have been widely investigated, also in search for better luminescent materials [2–8]. To keep the charge balance, simultaneously with lanthanide-ions, monovalent cations or/and silicate-ions are often inserted in the crystal lattice [7]. The substitution of Ca^{2+} by Ln^{3+} solely may result either in the cationic-vacancy formation or in the removal of the proton from the hydroxide-group. In majority of studies, the latter process is considered as most appropriate, with an end-composition $Ca_8Ln_2(PO_4)_6O_2$ [6–11]. Ln^{3+} occupies mostly Ca2-sites which form "walls" of the hexagonal channels filled with the OH^- and O^{2-} anions. It is essential, that even in case of La^{3+} which has slightly bigger ionic radius than Ca^{2+}, such a substitution narrows the hexagonal channel so that the distance between the Ca2-site and an intrachannel oxygen atom decreases, while the cell volume increases as expected [9]. This is explained by a stronger attraction of the Ca2-site cation to O^{2-} than to initial OH^-. A new IR band at 523 cm^{-1} arises on the doping, suggesting a distinct La^{3+}–O^{2-} bonding. Very similar structural results were obtained for the Bi for Ca substituted hydroxyapatite, a Raman and IR band at 630 cm^{-1} was presumably assigned to the Bi–O vibrations [12,13]. Another evidence of the strong metal–oxygen bond in hydroxyapatite is found for the Eu^{3+}-doped compound which exhibits an unprecedented luminescent spectrum [6]. The spectrum has been described using parameters characterizing extremely strong axial crystal field never observed in other Eu^{3+}-containing compounds. The formation of a single strong Eu–O bond has been also supported by the emergence of the corresponding Raman and IR band at 545 cm^{-1} attributed to the bond's stretching vibrations. Such a strictly axial crystal field acting on a paramagnetic Ln-ion has to invoke huge magnetic anisotropy. The latter is the major issue now in looking for new single-molecule-magnets with high energy barrier for spin reorientation [14–18]. Recently we have shown that a copper-ion entering into the hexagonal channel of a phosphate hydroxyapatite forms an unusual linear paramagnetic $[OCuO]^-$-anion at oxidative conditions [19,20]. This anion exhibits a giant *c*-axis magnetic anisotropy and slow spin relaxation with the energy barrier for spin reversal of up to 100 cm^{-1}, i.e. behaves like an efficient single-molecule magnet. Apparently the intrachannel oxygen atom strongly bonded to the copper atom is a source of such anisotropy. The previous discussion suggests that the intrachannel oxygen atom can form a bond also with the Ca2-site trivalent-metal atom, which justifies further investigation of this phenomenon.

In the crystal structure studies available, only an average M2-

* Corresponding author.
E-mail address: kazin@inorg.chem.msu.ru (P.E. Kazin).

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position partially occupied by Ln (or Bi) and Ca has been determined [7,9,12,13]. Therefore we may conclude that the actual Ln–O and Bi–O bond lengths are not estimated leaving open even a question whether they are close to the observed average (Ca,Ln)2-O distance, longer, or shorter than it. In this work we present the results on structural refinement of La- and Bi-for-Ca substituted apatites using high-resolution laboratory X-ray powder diffraction (XRPD) patterns and focusing on the determination of the individual La–O and Bi–O bond lengths. Among lanthanides, La looks the best for our purposes as it substitutes Ca in hydroxyapatite most readily: the substitution becomes more complicated with the decrease of the Ln-ion radius, so that the final stoichiometry is not reached starting from Sm [11]. And Bi, having nearly the same ionic radius as La, is able to form shorter and more covalent bonds with oxygen thereby representing a good choice for comparison in order to reveal to what extent the bond length is connected to the ion nature.

2. Experimental

Samples with nominal compositions $Ca_{10}(PO_4)_6(OH)_2$ (1), $Ca_9La(PO_4)_6O(OH)$ (2), $Ca_8La_2(PO_4)_6O_2$ (3), $Ca_9Bi(PO_4)_6O(OH)$ (4), $Ca_8Bi_2(PO_4)_6O_2$ (5) were prepared by high-temperature solid state reaction using chemically grade $CaCO_3$, $(NH_4)_2HPO_4$, Bi_2O_3 and freshly calcined La_2O_3. The reagents were grinded in an agate mortar, heated for 1 h to 600 °C, kept at this temperature for 1.5 h, heated further for 1 h to 800 °C and annealed for 3 h. The products were grinded and annealed several times at 1150 °C (**1–3**) or 1000 °C (**4**, **5**) for 3-6 h each with subsequent air-quenching and intermediate regrinding. Before the final annealing, the powders were pressed in pellets. The dopants La and Bi are also denoted as M in the further discussion. Samples **1–3** were analyzed for the presence of peroxide-ions using red-ox titration with KI and $Na_2S_2O_3$ described in [21]. Sample **1** contained peroxide in quantity corresponding to $5 \pm 0.5\%$ of the OH^- by $1/2\ O_2^{2-}$ substitution. Samples **2** and **3** contained only traces of peroxide (ca. 0.5% of the OH^- substitution).

High-precision XRPD was performed on a D8 Bruker-AXS powder diffractometer (Cu-Kα_1 radiation from a primary Ge(111) Johansson-type monochromator; Lynx-Eye position-sensitive detector with an opening angle of 3.5°) in Bragg-Brentano geometry in the 2θ range 10–120° with the increment of 0.0079° in 2θ. The samples were rotated during measurement for better particle statistics. The measurement time was chosen to obtain the main-peak counts number of the order of 10^5. The crystal structures were refined using Jana2006 program [22,23] in space group $P6_3/m$, $Z=1$. Other space groups-subgroups of $P6_3/m$ as well as $P2_1/b$- were also checked at the early stage of refinement, but no meaningful improvement of the R-factors and structure was achieved. Moreover, no superstructure reflection down to 0.1% of relative intensity was found. For most of the samples the line shape declined slightly from that fitted with one pseudo-Voigt function (with an appropriate asymmetry parameter). This became clearly visible due to high crystallinity of the samples and high resolution of the diffractometer. Such a situation we have often observed and consider originating from non-uniform dispersion of lattice parameter values due to formation of solid solutions such that the distribution of the values may be asymmetric and even bi- or polymodal. Probable reasons for the variation of the cell parameters are peculiar formation-decomposition processes of peroxide groups [21,24] as well as a non-uniform metal-cation substitution. In particular, in calcium apatite prepared at different annealing conditions in air, peroxide was found by a red-ox titration in quantities corresponding to 0–30% substitution of hydroxide by peroxide [25,26]. The above assumptions are in line with the fact that the line shape is quite different for different samples. Particularly for **3**, the line shape is very well described by a single pseudo-Voigt function. This sample is virtually saturated with La (see also Discussion) and one may expect a low dispersion of the La-content in the solid solution while the peroxide-ions are practically absent. In order to better access the line shape the patterns were fitted using two or three pseudo-Voigt functions with partially restricted parameters, which in fact meant two- or three-phase refinement with equal atomic parameters for these "phases". Cell parameters were then calculated as a weighted average of those obtained for every component ("phase"). This approach afforded to reduce R_{wp} by up to 40%. Minor deviations from the line shape might still remain after this procedure and be the source of somewhat increased Goodness-of-fit parameters.

All atomic positions were refined except hydrogen atoms. The metal-cation site occupancies were refined assuming that M substitutes Ca without forming cation vacancies. Anisotropic atomic displacement parameters (ADP's) were refined for all atoms situated in fully occupied positions. For split positions such as Ca2-La2, Ca2-Bi2, and intrachannel O4, isotropic ADP's were refined for Ca, La, and O, and anisotropic ones – for Bi. In case of Bi-containing apatites partial constrains to anisotropic ADP's of O1 and O2 were applied. The occupancy of O4 was found to vary within $\pm$ 2% of full occupation and hence was fixed to 0.5 in the final refinement. The identified impurity phases were included into refinement with fixed atomic parameters and overall ADP: $CaCO_3$ (2.5%) in **1**, $LaPO_4$ (5.7%) in **3**, and β–$Ca_3(PO_4)_2$ (1.6%) in **4**. In **5**, several unidentified reflections with intensities below 0.5% were observed and the corresponding small 2θ-intervals were cut out. Hydrogen atoms were not located and included into the refinements. In the chemical formulas, the index at hydrogen, 1-δ denotes that at such preparation conditions, a part of hydroxide-groups may be replaced by peroxide-groups [25,26]. Initial refinements were conducted considering the position of the channel-wall cation as a non-split one, i.e. with the same coordinates for Ca2 and M2. The final refinements were performed using individual positions for the calcium and the doping metal atoms. Standard deviations were calculated applying the Berar's factor, which yielded larger values considered as much more realistic. The accuracy might be even underestimated in this case.

To check the consistency of the "multi-phase" approach with the standard one, the XRPD patterns of **1**, **2**, **4**, and **5** were also refined using single pseudo-Voigt functions, which gave substantially larger reliability factors though (see Supplementary material). Most of the atomic parameter values obtained overlapped within one standard deviation with those refined applying several pseudo-Voigt functions, and all related interatomic distances differed by less than 0.02 Å. Below we will consider only the data obtained using the "multi-phase" approach as more precise ones.

Further details of the crystal structure investigations may be obtained from Supplementary material and from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fizkarlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository numbers 429746, 429747, 429748, 429749, 429750.

Raman spectra were registered on a RENISHAW in Via Reflex spectrometer (scanning range 100–1500 cm^{-1}, $\lambda=633$ nm). Fourier transform infrared spectra (FT-IR) were recorded on a Perkin Elmer Spectrum One FT-IR in the range 520–4000 cm^{-1}. Bond-valence (BV) calculations were conducted with a soft BV 0.96 program [27].

Diffraction patterns are presented in Figs. 1–5. Full list of atomic positional and displacement parameters is presented in Supplementary material, Table S1.

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