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Electron structure of apatite-like compounds with isomorphic substitution in tetrahedral positions

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Effect of isomorphic anionic substitutions in the apatite-like calcium structures on their electron structure has been investigated. Changes in the electron subsystem of the first synthesized compounds $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$ (where $M = F^-, Cl^-$, $x = 0, 1, 3, 5, 6$) caused by isomorphic anionic substitutions have been investigated using spectral and structural methods. It is established that fluorine and chlorine containing compounds are characterized by a general behavior tendency of the local electronic densities on calcium and oxygen atoms at the variation of anionic group number that evidences the electron structure independence of the anion type on the *c*-axis.

Исследовано влияние анионных изоморфных замещений в апатитоподобных структурах кальция на их электронное строение. Спектральными и структурными методами исследованы изменения в электронной подсистеме при изоморфных анионных замещениях впервые синтезированных соединений $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$, где $M = F^-$, Cl^-, $x = 0, 1, 3, 5, 6$. Установлено, что соединения с фтором и хлором характеризуются общей тенденцией поведения локальной электронной плотности на атомах кальция и кислорода при варьировании количества анионных групп, что свидетельствует о независимости электронной структуры от типа аниона на оси *c*.

Tetrahedral anion $(XO_4)^{3-}$ is a structural element in many crystalline compounds, in particular, in garnets, spinels, and apatites; as a rule, physico-chemical properties of compounds applied in practice are defined to a great extent by the tetrahedral sublattice [1, 2]. So, vanadates with the apatite structure are used in ionizing radiation dosimeters and as catalysts, while alkaline-earth metal hydroxyapatites are used as laser crystals, luminophors, and biocompatible materials [2–5]. Structural modification by isomorphic substitution in the tetrahedral sublattice causes considerable changes in physical properties of apatites [6, 7]. Consideration of literature data allows to conclude that the problem of isomorphic substitutions in the tetrahedral sublattice of fluoro- and chloroapatite has not been still investigated comprehensively enough by spectral methods that could provide the preconditions for spectrally directed synthesis of the isostructural compounds with planned design of properties [2].

In this work, influence of anionic isomorphic substitutions in the apatite-like calcium structures on their electron structure is investigated. For the first time compounds $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$ (where $M = F^-$, Cl^-, $x = 0, 1, 3, 5, 6$) with isomorphic anionic substitutions have been synthesized, and spectral and structural methods have been used to investigate the changes in the electron subsystem thereof. X-ray photoelectron spectra were obtained using a Series 800 XPS Kratos Analytical electron spectrometer with a non-monochromatic Al K_α (1486.6 eV) X-ray source. Energy resolution, defined as the full width at half-maximum of Ag $3d_{5/2}$-line, was 0.1 eV. The accuracy of binding energy determination was ≤0.1 eV. The electron binding energy E_b

was calibrated using standard C 1*s*-line of hydrocarbon electrons on the surface of the samples, E_b (C 1*s*) = 285.0 eV. Studied specimens of Ca-HAP and isomorphically substituted samples were finely dispersed powders, pressed into tablets.

Binding energies for core levels of studied compounds are shown in Table 1. To interpret the results, the data for isomorphically substituted calcium hydroxyapatite obtained before [8] were used. It is seen that at partial or complete substitution in $Ca_5(PO_4)_3F$, binding energy changes are observed for all electron levels of the atoms. The maximum of O 1*s* line remains essentially unshifted at substitution of one anionic group ($PO_4 \rightarrow VO_4$). The maximum in calcium 2*s* curve is shifted towards higher binding energy by 0.2 eV. The Ca $2p_{3/2}$ line is shifted towards higher binding energy by 0.1 eV while the Ca $2p_{1/2}$ line binding energy remains unchanged. The phosphorus 2*s* line is shifted towards lower binding energy by 0.3 eV while the P 2*p* line, by 0.2 eV in the same direction. Thus, small shifts in binding energy of calcium and phosphorus electron levels occurs at this substitution. Moreover, only levels with lower binding energy and located close to the valence band top are shifted.

Substitution of three anionic group in the $Ca_5(PO_4)_3F$ results in still greater changes in electron structure. O 1*s* electron binding energy is shifted towards lower energy by 0.2 eV that evidences appearance a new energy state of oxygen. The maximum of calcium 2*s*-curve does not changed its position, at the same time, Ca $2p_{3/2}$ and Ca $2p_{1/2}$ lines are shifted towards lower binding energy by 0.3 eV. The phosphorus 2*s* line is shifted towards lower binding energy by 0.3 eV. The P 2*p* line is shifted in the same direction by 0.1 eV. The V $2p_{3/2}$ line is shifted towards lower binding energy by 0.6 eV. At this point, apparently, we can suppose that the crystal lattice becomes somewhat "loosen" as the new oxygen positions appear. Still more considerable changes occur in the apatite electron structure due to substitution of five anionic groups. The O 1*s* line is shifted towards lower binding energy by 1.2 eV. Consequently, the new oxygen states have an appreciably higher negative charge on atoms that evidences considerable changes in the oxygen environment of Ca and V atoms in the compound crystal lattice. The 2*s* calcium line is shifted by 0.5 eV, and Ca $2p_{3/2}$ and Ca $2p_{1/2}$, by 0.4 eV shifts towards lower binding energy. The P 2*s* line is shifted by 0.2 eV and the P 2*p* one, by 0.1 eV towards lower binding energy. Shift of the V $2p_{3/2}$ line by 0.5 eV occurs in the same direction.

At partial or complete substitution in the $Ca_5(PO_4)_3Cl$, changes in binding energies are observed for all atoms, too, but those are more considerable. The maximum of O

Table 1. Electron binding energy E_b (eV) of core levels for studied compounds.

Compound	O 1*s*	Ca 2*s*	Ca $2p_{3/2}$	Ca $2p_{1/2}$	P 2*s*	P 2*p*	V $2p_{3/2}$
$Ca_{10}(PO_4)_6(OH)_2$	531.2	439.2	347.3	–	–	133.3	–
$Ca_{10}(PO_4)_5(VO_4)(OH)_2$	531.2	439.2	347.3	–	–	133.4	517.6
$Ca_{10}(PO_4)_3(VO_4)_3(OH)_2$	531.0	439.0	347.2	–	–	133.2	517.4
$Ca_{10}(PO_4)(VO_4)_5(OH)_2$	530.2	438.8	346.8	–	–	132.8	517.0
$Ca_{10}(VO_4)_6(OH)_2$	530.1	438.7	346.8	–	–	–	517.0
$Ca_5(PO_4)_3F$	531.5	439.2	347.5	351.1	191.1	133.6	–
$Ca_{10}(PO_4)_5(VO_4)F_2$	531.4	439.4	347.6	351.1	190.8	133.4	517.6
$Ca_{10}(PO_4)_3(VO_4)_3F_2$	531.3	439.2	347.2	350.8	190.8	133.5	517.0
$Ca_{10}(PO_4)(VO_4)_5F_2$	530.3	438.7	347.1	350.7	190.9	133.5	517.1
$Ca_5(PO_4)_3Cl$	531.7	439.2	347.6	351.2	191.0	133.5	–
$Ca_{10}(PO_4)_5(VO_4)Cl_2$	531.2	439.2	347.4	351.0	190.8	133.6	–
$Ca_{10}(PO_4)_3(VO_4)_3Cl_2$	531.2	439.2	347.7	351.2	190.6	133.3	517.7
$Ca_{10}(PO_4)(VO_4)_5Cl_2$	530.3	439.1	347.1	350.7	190.5	133.5	517.3
$Ca_5(VO_4)_3Cl$	530.1	438.8	347.0	350.5	–	–	517.2

E_b values are given relatively to E_b (C 1*s*) = 285.0 eV. Accuracy of measurement ±0.1 eV.

1*s* line at substitution of one anionic group ($PO_4 \rightarrow VO_4$) is shifted towards lower binding energy by 0.5 eV that evidences the appearance of a new energy state for oxygen, as well as in the case of calcium fluoro-apatite. The maximum of calcium 2*s* curve remains unshifted, while Ca $2p_{3/2}$ and Ca $2p_{1/2}$ lines are shifted towards lower binding energy by 0.2 eV. The phosphorus 2*s* line is shifted towards lower binding energy by 0.2 eV. The P 2*p* line is shifted towards lower binding energy by 0.1 eV.

Substitution of three anionic group in the $Ca_5(PO_4)_3Cl$ gives rise to the shift of O 1*s* line towards lower binding energy by 0.5 eV. The maxima of calcium 2*s* and $2p_{1/2}$ curves remain unshifted, while Ca $2p_{3/2}$ is shifted towards higher binding energy by 0.1 eV. The phosphorus 2*s* line is shifted towards lower binding energy by 0.4 eV and P 2*p*, by 0.2 eV. These changes, similar to the case of calcium phosphate-vanadate, are connected most likely with "loosening" of the crystal lattice at appearance of new oxygen positions [8]. At substitution of five anionic groups, the O 1*s* line is shifted towards lower binding energy by 1.4 eV. The maximum of calcium 2*s* curve is shifted towards lower binding energy by 0.1 eV, while Ca $2p_{3/2}$ and Ca $2p_{1/2}$, by 0.5 eV. The phosphorus 2*s* line is shifted towards lower binding energy by 0.5 eV. The P 2*p* line remains unshifted and V $2p_{3/2}$ is shifted towards lower binding energy by 0.4 eV. The substitution of six anionic groups gives rise to further decrease in binding energy of oxygen, calcium, and vanadium electrons. The O 1*s* line is shifted towards lower binding energy by 1.6 eV. Thus, similar to the case of calcium phosphate-vanadate, the new oxygen states bear an appreciably higher negative charge on the atoms, that indicates significant changes in the oxygen environment of Ca and V atoms in the compound crystal lattice. The maximum of calcium 2*s* curve is shifted towards lower binding energy by 0.4 eV, while Ca $2p_{3/2}$ and Ca $2p_{1/2}$, by 0.6 and 0.7 eV, respectively, and V $2p_{3/2}$, by 0.5 eV.

Thus, for two different series of fluorine and chlorine containing compounds, a common behavior tendency of local electron density on calcium and oxygen atoms is observed at a variation of anionic group number, evidencing that the electron structure is independent of anion type on the *c*-axis. The most significant decrease of binding energy amounting 1.6 eV is observed for O 1*s* electrons of $Ca_5(VO_4)_6Cl$ compound. It is possible to explain this change to that at the prevailing content of vanadate tetrahedrons, the internal electronic level emerges due to the electron density increase.

Table 2. Lattice parameters of studied compounds.

Compound	*a*, Å	*c*, Å
$Ca_{10}(PO_4)_6(OH)_2$	9.424	6.879
$Ca_{10}(PO_4)_5(VO_4)(OH)_2$	9.492	6.903
$Ca_{10}(PO_4)_3(VO_4)_3(OH)_2$	9.619	6.924
$Ca_{10}(PO_4)(VO_4)_5(OH)_2$	9.730	6.984
$Ca_{10}(VO_4)_6(OH)_2$	9.768	7.003
$Ca_5(PO_4)_3Cl$	9.52	6.85
$Ca_{10}(VO_4)(PO_4)_5Cl_2$	9.666	6.826
$Ca_{10}(VO_4)_3(PO_4)_3Cl_2$	9.864	6.821
$Ca_{10}(VO_4)_5(PO_4)Cl_2$	10.072	6.799
$Ca_{10}(PO_4)_6F_2$	9.370	6.883
$Ca_{10}(PO_4)_5(VO_4)F_2$	9.400	6.900
$Ca_{10}(PO_4)_3(VO_4)_3F_2$	9.552	6.950
$Ca_{10}(PO_4)(VO_4)_5F_2$	9.653	6.991
$Ca_{10}(VO_4)_6F_2$	9.67	7.01

As to fluorine containing samples, a different behavior in position changes of vanadium V $2p_{1/2}$ and V $2p_{3/2}$ electron levels is observed. As anionic groups PO_4 are substituted by VO_4, the binding energy of V $2p_{1/2}$ level increases and that of V $2p_{3/2}$ one decreases, that is explained by the different nature of lone *d*-electron density on vanadium atoms. For binding energy of the P 2*p* level, the changes are insignificant both in calcium fluoro- and chlorovanadate-phosphate apatites and amount approximately 0.5±0.1 eV in calcium vanadate-phosphate hydroxyapatites. Distinctions are observed only for binding energy of P 2*s* level which decreases insignificantly in calcium vanadate-phosphate fluorapatites (by 0.2 eV), while for calcium vanadate-phosphate chlorapatites, this decrease is essential (about 0.5±0.1 eV), that seems to be connected with a change in the spatial organization of these crystals at concentration changes of phosphate tetrahedrons (Table 2).

From the *c*/*a* ratio for investigated compounds, it is seen (Fig. 1) that the change of structural parameters is essentially the same both for vanadate-phosphate fluorapatites and vanadate-phosphate hydroxyapatites. However, for vanadate-phosphate chlorapatite, a significant change in struc-

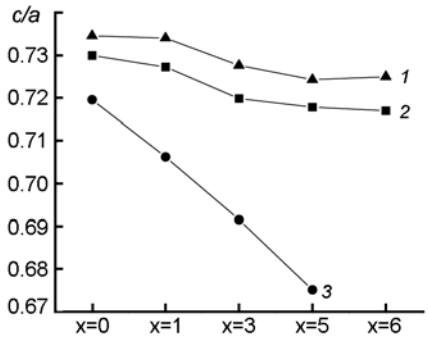

Fig. 1. The c/a ratio of lattice parameters for the studied compounds $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$ for M: *1* – F, *2* – OH, *3* – Cl.

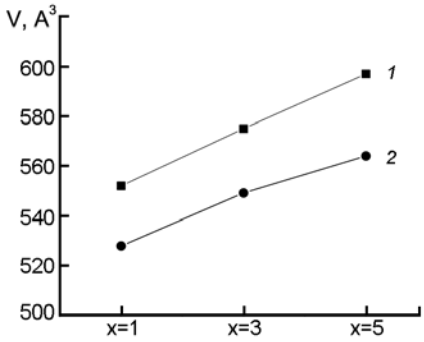

Fig. 2. Change of the crystal unit cell size for studied compounds $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$ for M: *1* – Cl, *2* – F.

tural parameters is observed with increase in vanadate tetrahedron concentration, that, most likely, is connected with symmetry decrease within limits of the mirror plane. A chloride ion, when substituting an OH^- ion, will penetrate into the plane of calcium ions "more deeply" than an ion OH^- due to presence of a sixth order rotation axis [2]. Whereas chloride ions do not arrange equidistantly between the planes occupied by calcium ions, the structure loses elements of mirror plane symmetry and, thus, the symmetry decreases, that correlates with decreased binding energy of core levels in calcium vanadate-phosphate chlorapatite. It follows from change curves of the crystal unit cell size for studied compounds (Fig. 2) that at a gradual isomorphic substitution by vanadate tetrahedrons, a general tendency to increase in the unit cell volume is observed. Moreover, for chlorine-containing samples the cell volume is by about 25 Å^3 larger, that it is possible to explain by the size difference between chlorine and fluorine atoms (the atomic radius for fluorine is 0.50 Å, for Cl, 1 Å).

Thus, the prevailing content of vanadate tetrahedrons in the calcium vanadate-phosphate chloro- and fluoroapatite results in that the internal electron levels of calcium and phosphorus emerge due to increase of electronic density. Fluorine- and chlorine-containing compounds $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$ (where $x = 0, 1, 3, 5, 6$; $M = F^-, Cl^-$) are characterized by a common behavior trend of local electron density on calcium and oxygen atoms at variation of anionic group number, that testifies to electron structure independence of anion type on a c-axis. For calcium vanadate-phosphate chloroapatite, a significant change of structural parameters is observed with increasing concentration of vanadate tetrahedrons, that correlates with the obtained XPS data. The different behavior in changes of vanadium electron levels positions V $p_{1/2}$ and V $2p_{3/2}$ for fluorine- and chlorine-containing samples is explained by behavior differences of lone d-electron density on vanadium atoms.

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Електронна будова апатитоподібних сполук з ізоморфним заміщенням у тетраедричних позиціях

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Досліджено вплив аніонних ізоморфних заміщень у апатитоподібних структурах кальцію на їх електронну будову. Спектральними та структурними методами досліджено зміни у електронній підсистемі вперше синтезованих сполук $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$ (де $M = F^-$, Cl^-, $x = 0, 1, 3, 5, 6$) при ізоморфних аніонних заміщеннях. Встановлено, що сполуки з фтором та хлором характеризуються загальною тенденцією поведінки локальної електронної густини на атомах кальцію та кисню при варіюванні кількості аніонних груп, що свідчить про незалежність електронної структури від типу аніона на осі *c*.