

Physics and Mathematics Sciences

UDC 535.33/34:539.216./22

Kasyanenko Vasyl

PhD in Physics and Mathematics, Professor

Касьяненко Василий Харитонович

кандидат физико-математических наук, профессор

Касьяненко Василь Харитонович

кандидат фізико-математичних наук, професор

Burdeynyuy Volodymyr

PhD in Physics and Mathematics, Associated Professor

Department of General Physics

Vinnitsia National Technical University

Бурдейний Володимир Мефодійович

кандидат фізико-математичних наук, доцент

Кафедра загальної фізики

Вінницький національний технічний університет

Бурдейный Владимир Мефодьевич

кандидат физико-математических наук, доцент

Кафедра общей физики

Винницкий национальный технический университет

**ELECTRONIC STRUCTURE AND PROPERTIES OF APATITE-LIKE
CALCIUM-BASED COMPOUNDS, INITIATED BY NANODIMENSION,
BIOGENIC FACTOR AND ISOMORPHIC SUBSTITUTION OF
CALCIUM BY 3D-METALLS**

**ЕЛЕКТРОННА БУДОВА І ВЛАСТИВОСТІ АПАТИТОПОДІБНИХ
СТРУКТУР НА ОСНОВІ КАЛЬЦІЮ, ІНІЦІЙОВАНІ**

**НАНОРОЗМІРНІСТЮ, БІОГЕННИМ ЧИННИКОМ І
ІЗОМОРФНИМИ ЗАМІЩЕННЯМИ КАЛЬЦІЮ ЗД-МЕТАЛАМИ
ЭЛЕКТРОННОЕ СТРОЕНИЕ И СВОЙСТВА АПАТИТОПОДОБНЫХ
СТРУКТУР НА ОСНОВЕ КАЛЬЦИЯ, ИНИЦИИРОВАННЫЕ
НАНОРАЗМЕРНОСТЬЮ, БИОГЕННЫМИ ФАКТОРАМИ И
ИЗОМОРФНЫМ ЗАМЕЩЕНИЕМ КАЛЬЦИЯ ЗД-МЕТАЛЛАМИ**

Summary. Calcium apatites due to their physicochemical properties, high biological activity deservedly attract special attention not only in view of purely scientific interest, but also in connection with the use of drugs synthesized on their basis. in practical traumatology. dentistry, i.e. in those areas of medicine that are relevant to the treatment and restoration of bone tissue. As a rule, the basic elements are samples of nanometric dimensions. Electronic properties, features of chemical bond, structural parameters demonstrate high sensitivity to size reduction. In this paper, the nature of chemical bond, redistribution of electron density in energy and real space, isomorphically substituted hydroxyapatites based on calcium are studied with the complex application of such methods as photoelectron and X-ray spectroscopy, nuclear magnetic resonance, atomic force spectroscopy.

Key words: calcium apatites, isomorphic substitution, chemical bond, electronic spectrum, density of states.

Анотація. Кальцієві апатити завдяки своїм фізико-хімічним властивостям, високій біологічній активності цілком заслужено привертають особливу увагу не тільки з огляду на чисто науковий інтерес, але і в зв'язку із застосуванням препаратів, синтезованих на їх основі. у практичній травматології. стоматології, тобто у тих галузях медицини, які мають відношення до лікування та відновлення кісткових тканин. Як правило, базовим елементом є зразки нанометричних розмірів. Електронні властивості, особливості хімічного зв'язку, структурні

параметри демонструють високу чутливість щодо редуції розмірів. В даній роботі із комплексним застосуванням таких методів, як фотоелектронна і рентгенівська спектроскопія, ядерний магнітний резонанс, атомно-силова спектроскопія вивчається природа хімічного зв'язку, перерозподіл електронної густини в енергетичному та реальному просторі, ізоморфно заміщених гідроксоапатитів на основі кальцію.

Ключові слова: кальцієві апатити, ізоморфне заміщення, хімічний зв'язок, електронний спектр, густина станів.

Анотація. Кальциевые апатиты благодаря своим физико-химическим свойствам, высокой биологической активности вполне заслуженно привлекают особое внимание не только из-за чисто научного интереса, но и в связи с применением препаратов, синтезированных на их основе. в практической травматологии. стоматологии, то есть в тех областях медицины, которые имеют отношение к лечению и восстановления костных тканей. Как правило, базовым элементом являются образцы нанометрических размеров. Электронные свойства, особенности химической связи, структурные параметры демонстрируют высокую чувствительность к редуции размеров. В данной работе с комплексным применением таких методов, как фотоэлектронная и рентгеновская спектроскопия, ядерный магнитный резонанс, атомно-силовая спектроскопия изучается природа химической связи, перераспределение электронной плотности в энергетическом и реальном пространстве, изоморфно замещенных гидроксоапатитов на основе кальция.

Ключевые слова: кальциевые апатиты, изоморфное замещение, химическая связь, электронный спектр, плотность состояний.

Introduction. The problems of environmental safety and human health, extending life expectancy and vital necessity to spread human civilization

beyond the our planet have become the main challenge for humanity at the beginning of the current millennium. In this context one of the most fundamental tasks is to research and develop technologies for creation and production of materials promising with point of view their biomedical and environmental applications. Concerning the level of publications and scale of undertaken in the area research apatite and apatite compounds occupy one of the most notable place.

Natural minerals and synthetic compounds with apatite type structure form a wide variety of chemical systems, namely $M_{10}(XO_4)_6Y_2$ where $M = Ca, Sr, Ba, Pb$; $X = P, V$; $Y = OH, F, Cl$. The high tolerance to living tissue, along with the peculiarities of electron and crystalline structure of apatite-like compounds, determine their direct impact on technical, environmental and biological applications. Materials based on apatite-like compounds are already being used in a number of computer devices, for creation of quantum generators, in the field of communication means, power engineering, nanomedicine, nanobionics, etc.

One of the wide used methods to control the physical and chemical properties of a substance is isomorphic substitution. Targeted synthesis of compounds with the demanded and reproducible properties requires knowledge of the electronic structure formation regularities, in their dependence on composition, technological conditions of synthesis, changes in the dimensions and elements topology. It is necessary to add that relationship between the composition features and chemical and electron structure have to be taken in account in order to realize the above mentioned purposes.

It is quite clear that understanding of nanostructures organization can not be complete and settled without the extensive use of new physical methods to study substances of interest and wide applications of quantum mechanical treatment of their electronic structure and properties. In this work in order to correct and unambiguous interpret the obtained experimental results a

comprehensive approach has been applied. It consists in combined use of advanced methods to investigate electron structure, surface morphology and physical properties.

As it is well known a reduction of substances to the nanometer scale leads to appearance of new properties different from ones that correspond to both atoms and condensed matter state. To date, the noted change in these properties is clearly expressed among others for apatite and apatite-like compounds of nanoscale size. The most expected progress of such substances applications is directly related to nano-size apatite samples investigations. Accordingly to a number of reviews calcium hydroxoapatite turns out effective material to produce medicines for fractures treatment or bone tissues defects. Thus studies of physical and chemical properties of apatite with biogenic nature become not only very interested but also vital necessary.

Here are represented main results of investigations of minerals and synthetic compounds with structural type of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ by X-ray photoelectron spectroscopy, X-ray spectroscopy, nuclear magnetic resonance high-vacuum microscopy of atomic forces methods applying.

1. Electron structure of isomorphically substituted apatites and morphology of calcium hydroxapatite.

As it follows from numerous references the isomorphic substitutions allow to significantly affect the physical properties of apatites. The study of crystal ensembles modified by this treatment gives information about the nature of acting forces, the impurities distribution and their localization as well as mechanisms of influence of determined structural changes on the solid state systems significant properties. In this context research of chemical bonds specificity and electron states peculiarities of apatite-like compounds due to their decisive impact on physical properties become not only important but also really urgent.

The results of studies of calcium apatite electronic structure reconstruction due to the isomorphous replacement of calcium ions by nickel ions, and the results of the practical applications based on nanodispersed calcium apatites set properties arouse growing interest to them in terms of generally accepted medical practices. The therapy efficiency is not least associated with peculiarities of physical and chemical processes of above mentioned compounds accumulation by apatite-containing bone tissues of living organisms including humans.

Our dates show that the $K\beta_{2,5}$ spectra of calcium contained in stoichiometric hydroxoapatite and the same spectra relative to hydroxoapatite with various levels of isomorphous substitution of calcium by 3d metals has manifested considerable similarity of spectra nearly the main maximum and significant discrepancy in the long-wavelength region. This fact can be explained by strengthening of PO_4^{3-} oxygen matrix chemical bond with metall atoms and weakening the $Ca(Ni)-O-Ca(Ni)$ bodns along the hexagonal axis.

In calcium hydroxapatite isomorphous substitution of calcium ions by ones of 3d-metal, namely magnesium, and strontium modifies insignificantly the structure of the valence band occupied part. This energy region preserves a pronounced band character with different widths of individual subbands, that is the upper part of the valence band and the lower part of the same band. The dominant contribution to the main features of the valence band upper part formulation is associated with the hybridized s-, p-, and partially d-electron states of the metal and phosphorus ions. The structure of the subvalent states is determined by the s-states of oxygen and phosphorus (See Fig. 1).

The form of the main maximum of the K-band of calcium is mainly determined by the features of F and G, which are formed by the d- and p -states of calcium and the short-wave maximum of H, which is mainly related to the manifestation of the p -states of oxygen and d-states of calcium (Fig. 1). The splitting of the K-band main maximum of calcium in HAP takes place due to

presence of two, namely, Ca(1) and Ca(2), its crystallographic positions. As for as the F and G bands of complete density of states their general features are formed by p-states of oxygen. mainly. Beside it the hybridization of the p-, d-states of calcium and the p-states of phosphorus and oxygen contribute to form of the G-band some significant peculiarities.

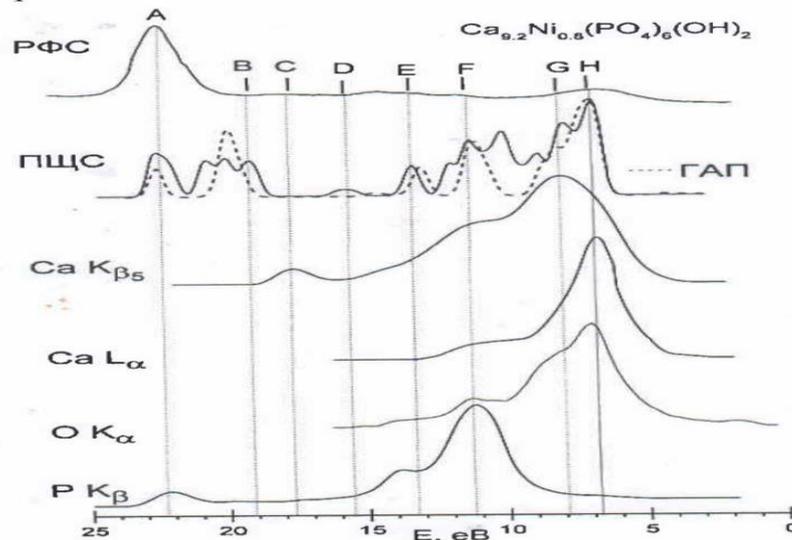


Fig. 1. The X-ray spectra of isomorphically substituted hydroxoapatite (HAP) combined on a single energy scale and complete densities of states

For isomorphic substitution of calcium ions by nickel simultaneous increase in binding energy from both O1s and core levels of calcium has been observed. This fact points out that as for as complete balance in chemical bonds covalent component plays dominant role. In the same time the isomorphic substitution of calcium ions by atoms of 3d metal, namely, magnesium or strontium, in the all apatite structures for a wide dopant concentration range leads to a decrease of electron density in calcium and oxygen atoms that maybe can indicate on increase in the covalent component proportion in the total balance of the chemical bond.

Beside it effects in the evolution of valence bands and charge states of atoms due to type and level of stoichiometric HAP matrix doping by the 3d metals, magnesium and strontium, are determined. Undertaken correlation in positions and shape of spectral lines with experimental data and results of

numerical evaluations indicates the predominant of dopant ions implantation in apatite structure instead of Ca(2). The oxygen tetrahedra sublattice, as well as in stoichiometric apatite, plays leading role in providing observed form and features of the complete electron states density in isomorphically substituted calcium apatites.

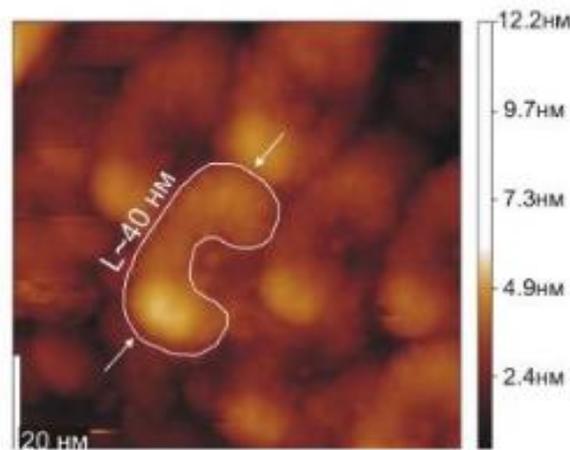


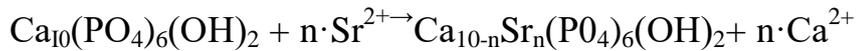
Fig. 2. Morphology of nanodispersed hydroxapatite morphology

One of the important factors affecting the inherent properties of a substance is its structural state. In this work, we obtained nanodispersed calcium apatite with a specific surface area about 500 m² / g by applying the method of sol-gel. The morphology of synthesized samples of calcium nanodispersed apatite was investigated by the method of high vacuum probe microscopy of atomic forces with atomic resolution (Fig. 2). It is found that the average particle size is ~ 40 nm and one can also observe well pronounced characteristic shape and tendency to needle texture of apatite particles formation.

2. Sorption capacity of hydroxapatite based on ⁹⁰Sr

We have found the high sorption capacity of ⁹⁰Sr and water molecules in relation to the nanodispersed calcium apatite. We suppose that small particle sizes as well as non-stoichiometric structure are responsible for this effect. In addition has been also discovered that the Sr²⁺ cations plays role of inhibitors in calcium apatite dissolution. Thus we assume the suggestion that isomorphous

substitution of Ca^{2+} ions by ions Sr^{2+} of strontium takes place on the surface of the HAP. The process occurs accordingly to the scheme:



Formed by the above given scheme Sr²⁺-substituted apatite determines the rate of dissolution of calcium apatite. As the object of study the nanodispersed calcium apatite has been chosen and we examined five samples. Four of them numbered from 1 to 4 having weight 0,1 mg each (particle size was about 40 nm) were poured over with 10 ml of an aqueous solution with various concentrations of $^{90}\text{SrNO}_3$. The phase ratio was 1: 100. The sample №5 was prepared according to the following scheme: the initial gel weighing 1 g was poured over with 25 ml of calibrated solution with the same concentration of ^{90}Sr that was used for the sample №4. Then the colloidal solution of HAP was periodically stirred during 24 hours after which it was filtered by applying the Buchner funnel. After that, the degree of sorption and desorption of ^{90}Sr by apatite samples №1-4 were measured. As for the solid phase of the sample №5 this was subjected to heating at a temperature 650 ° C.

Increasing the concentration of radioisotope in water does not lead to a noticeable increase in distribution coefficient, although the desorption index with increasing of concentration shows almost linear increase (Table 1). Hence, a significant amount of absorbed radioisotope is easily desorbed from nanodispersed apatite. However under the same initial concentrations of ^{90}Sr in solution, the sorption characteristics of sample №5 are reduced by almost 35% in comparison with nanodispersed samples №1-4, and the desorption rate is reduced by about 30 times. Thus, the ^{90}Sr radioisotope adsorbed by nanodispersed apatite is strongly retained by its structure during the thermal conversion of HAP to crystallized state.

Table 1

Sorption characteristics of the studied samples in relation to ^{90}Sr .

N^o of sample	Carried in, Bc/ml	K_d, ml/g	desorbed, Bc/ml
1	5.4	285	3.8
2	9.3	389	6.9
3	30.0	206	20.8
4	61.0	279	42.0
5	61.0	183	1.48

The high values of desorption for nanodispersed sediments (Table 1) indicate that Sr^{2+} ions form weak bonds with the apatite structure. Perhaps they become adsorbed by surface instead of OH groups protons and / or create $\text{Sr}^{2+} \cdot n\text{H}_2\text{O}$ aquacomplexes. Thermal treatment of the initial ^{90}Sr -enriched precipitate conducts to the sharp decrease in magnitude of desorption under sufficiently high value of the coefficient K_d . This fact indicates that isomorphic implantation of weakly bounded with the surface nanosized particles of Sr^{2+} ions into the apatite structure takes place during the formation of large-sized apatite crystals under special regime of heating.

3. Investigation of apatites by NMR and RFES

In the study of samples of natural origin apatites by NMR with ^{31}P nuclei, a decrease in electron density on phosphorus atoms was observed. A slight shift was observed for the apatite of native bone and to a much greater extent for the mineral apatite (Fig. 3). Such behavior of the nature of the chemical bond in natural apatites may be explained by the imperfection of the structure of natural origin apatite, which causes the deformation of PO_4 -tetrahedra. Such deformations can be confirmed by a significant extension of the line ^{31}P of the MAS NMR spectrum, as well as by an increase in the half-width of the core energy ls-level of oxygen of natural origin apatite.

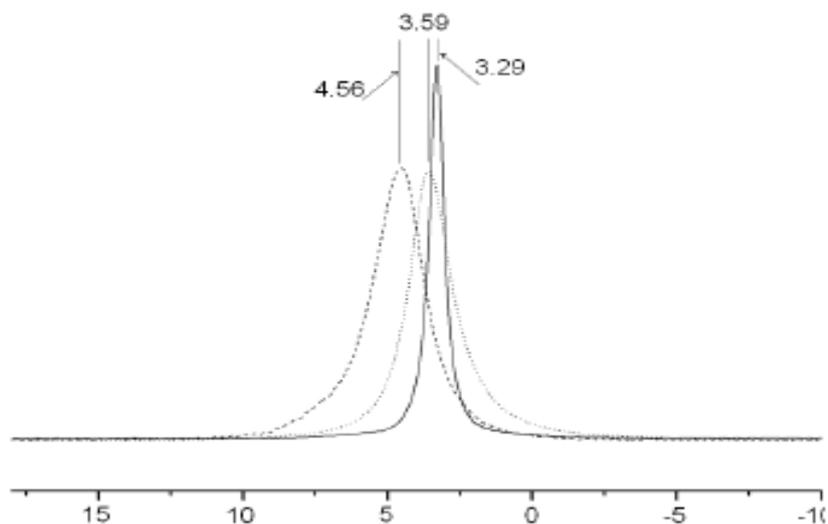


Fig. 3. ³¹P MAS NMR spectrum of samples: - synthetic apatite, mineral apatite, native bone

This indicates that the charge state of phosphorus is different for samples of natural and synthesized apatite. According to the table (Table 2), binding energy of the core 2p-level of phosphorus contained in natural apatite indicates a decrease in electron density on the phosphorus atom. At the same time as the charge on phosphorus atom decreases, one can observe some increase of the electron density on oxygen atoms, which is confirmed by the increase of the binding energy for 1s electrons of oxygen.

Table 2

Bond energy of the core electrons in a synthetic, natural Ca-HAP crystal and a native bone mineral

substance	Ca2P1/2	Ca2P3/2	P2p	O1s
Ca ₁₀ (PO ₄) ₆ (synthetic)	351,2	347,5	133,3	532,4
Ca ₁₀ (PO ₄) ₆ (natural)	351,2	347,4	133,4	532,5
Native bone mineral	351,2	347,4	133,4	532,4

The decrease in electron density on phosphorus atoms is confirmed by applying the method with a much higher resolution, namely the nuclear magnetic resonance on ³¹P nuclei. The data of the NMR approach, represented

by Fig.3 and 1, show that, both for native bone and to a greater extent for mineral apatite, the increase in chemical shift takes place indicating by this fact some reduction of external magnetic field screening by phosphorus atom electron shells. This effect points out a decrease in electron density on phosphorus atoms. Such redistribution of electron density between phosphorus and oxygen may indicate that ionicity degree of chemical bond phosphorus with oxygen in the apatite of natural origin is slightly higher than in the synthesized sample and turns out significantly higher for native bone pointing out a significant increase in ion component in the crystal as a whole (1). Indicated change in peculiarities of the chemical bond can be explained by imperfection of the structure of natural origin apatite, which is accompanied by deformation of PO_4 - tetrahedrons.

The valence electron density of calcium is formed mainly by Ca3d-states, whose electron density suffers significant decrease with growth of distance from the nucleus (Fig.4).

For the phosphorus atoms the electron density of the valence band unoccupied part, mainly formed by P3p-states, accordingly to our results manifests an anomalous spatial distribution. Directly near the nucleus the electron density of unoccupied part of the valence band in the vicinity of phosphorus atom is so small that it can be neglected. The electron density achieves maximums at some distance from nucleus of the atom along the lines connecting the phosphorus atoms with the centers of the oxygen faces, which are along the lines finding at the maximum distance from the P-O chemical bonds.

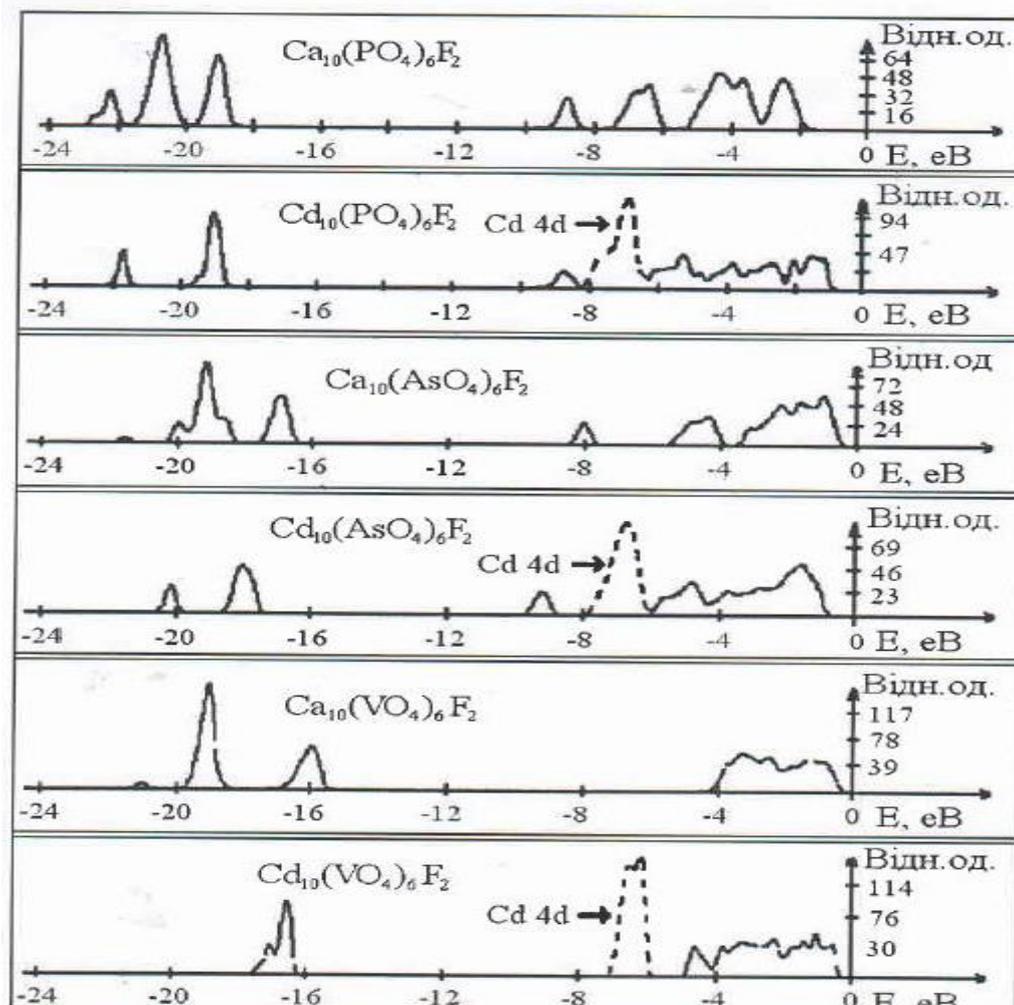
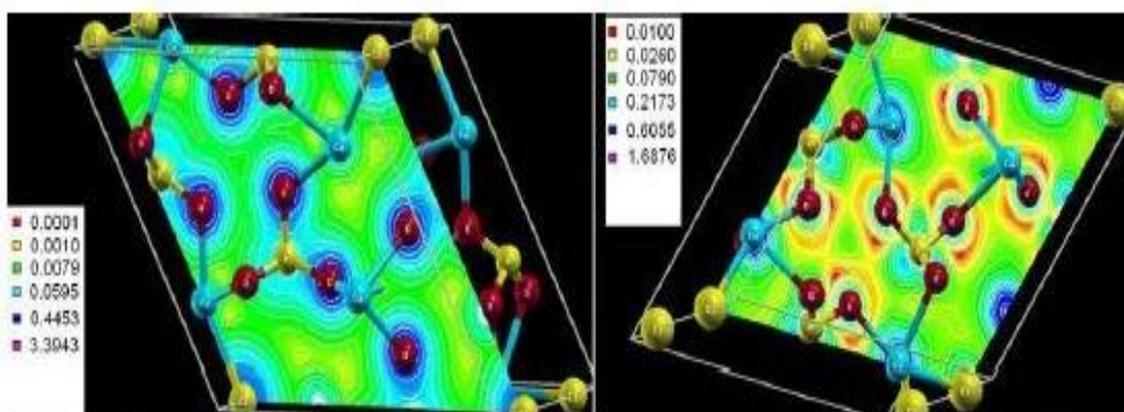


Fig. 4. Complete density of states (CDS) of calcium and cadmium fluoroapatites

The results of ΔE (NOMO-LUMO) for calcium phosphate apatites (Fig.5), determined by using the full-potential LDPH + LO method, can be considered satisfactory, because the difference between experimental and theoretical data does not exceed 0.3 eV, although for cadmium fluoroapatite, a notable deviation of the GGA gap from experimental date was observed. Transiting from $\text{Ca}_{10}(\text{P}_4\text{O}_4)_6\text{F}_2$ to $\text{Ca}_{10}(\text{P}_4\text{O}_4)_6(\text{OH})_2$, the energy gap decreases in 0.5 eV, that can be explained by appearance of electronic H 1s and O (OH) 2p- states in the vacant part of valence band. At the same time the passage from $\text{Ca}_{10}(\text{P}_4\text{O}_4)_6\text{F}_2$ to $\text{Ca}_{10}(\text{P}_4\text{O}_4)_6\text{Br}_2$ is accompanied by a considerable decrease, in almost 1.5 eV, of the gap width caused due to appearance of Br valence band 4p-states nearly the "pre-Fermi" region. The decrease in the width of the gap by

about 1 eV during the transition from calcium phosphate to calcium vanadate apatites is caused by the appearance in the unoccupied part of the valence band



V 3d-states.

Fig. 5. Spatial distribution of electron density in the "pre-Fermi region" in the energy range E (NOMO-LUMO-12eB) for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$

Table 3

Energy gaps of apatites

substance	ΔE (HOMO-LUMO), eV (calculated)	Energy gap, eV (experiment)
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	5.6	5.9
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	5.4	5.6
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	5.3	5.4
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	2.6	5.4
$\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$	2.5	-
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	2.3	-

The value of the calcium apatites energy gap (Table 3) is correctly described within the GGA approximation, whereas for cadmium apatites the same approximation significantly reduces the width of the energy gap. For cadmium apatites, the width of the energy gap completely correlates with the electronegativity of the anion located on the axis of the sixth order. It can be seen that as soon as electronegativity of the anion X decreases, the reduction of the energy gap takes place. In the series of "vanadate apatites" → "arsenate

apatites" → "phosphate apatites" the effective charges of valence electrons of oxygen ions increase. The calculation of the electron density at the nucleus of oxygen atoms averaged over all non-equivalent positions for the compounds $\text{Ca}_{10}(\text{VO}_4)_6(\text{OH})_2$, $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ gives the values 91.34, 91.25 and 89.96 \AA^{-3} respectively, which is in accordance with the experimental binding energies of the O 1s levels. Thus in a sequence of calcium apatites "vanadate" → "arsenate" → "phosphate", the spatial localization of the valence electron density of oxygen ions decreases in close vicinity of nuclei. The theoretically calculated X-ray emission bands of the compounds studied here turn out in good agreement in with the experimental data (Fig. 6).

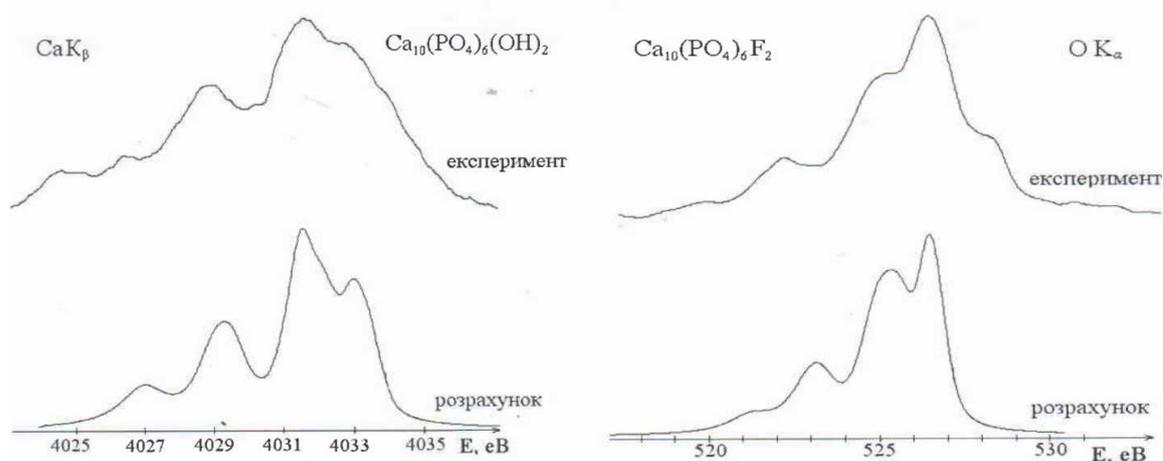


Fig. 6. Calculated and experimental X-ray emission bands of calcium phosphate apatites

Applying a treatment based on the energy approach, one can show that $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ belong to spatial group $P6_3/m$ instead of group $P6_3$. At addition a significant change in the nature of the Ca – O interaction because of the transition from phosphate apatites to vanadate analogues has been detected. Comparing vadanate apatites with their phosphate analogues shows an increase in the spatial localization of the electron density of calcium and oxygen at the direct vicinity of nuclei. As it has been determined for calcium apatites in the series of $\text{Ca}_{10}(\text{PO}_2)_6\text{X}_2$, where X = F, SI, Br OH, at the contrary to cadmium analogues the interactions XS-Os (PO_4) and Xp-O2p(PO_4), where X is a halogen or oxygen atom of a hydroxyl group atom play really notable role.

The charge transfer from calcium atoms to oxygen atoms is much greater in calcium apatites than from cadmium atoms to oxygen atoms in cadmium apatites. The average charge of calcium ions in compounds $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where $Z = \text{P, V or As}$, and $X = \text{F, SI, Br, OH}$ is equal to +1.61 of the electron charge while of the cadmium ions charge in apatite $\text{Cd}_{10}(\text{Z}_4)_6\text{X}_2$ where $Z = \text{P, V, As}$, and $X = \text{F, SI, Br, OH}$ is about +1.37 of the same electron charge. The charge of metal ions changes little when the type of anion located on the sixth-order axis changes, although the redistribution of the electron charge between the first and second non-equivalent positions takes place. At the same time decrease in the electronegativity of the anion situated on the sixth-order axis is accompanied by an increase in the charge of the Me(1) ion and a decrease in the charge of the Me(2) ion .

The transition from the apatites $\text{Ca}_{10}(\text{Z}_4)_6(\text{OH})_2$ where $Z = \text{P, V or As}$ to their cadmium analogues is accompanied by a small increase in the ionic charge of hydrogen and a significant decrease in the volume occupied by the H atom. The last fact can be treated as the result of some decrease in the elementary cell dipole moment along the c-axis, while the first of the facts demonstrates a considerable change in the nature of the O-H interaction due to the above appointed substitutions. Also the substantial spatial localization of Cd 4-d states at the direct vicinity of the nuclei is observed, while energetically these states are localized nearly at the "preFermi region".

Taking in account an insignificant change of the PO_4 tetrahedrals volume we can conclude that the PO_4 – tetrahedron shows high resistance against transition from one type of apatite to another. At the same time the tetrahedral form distortion of PO_4^{3-} ion decreases along the series $\text{Me}_{10}(\text{PO}_4)_6\text{Cl}_2 \rightarrow \text{Me}_{10}(\text{PO}_4)_6\text{F}_2 \rightarrow \text{Me}(\text{PO}_4)_6(\text{OH})_2$, where $\text{Me} = \text{Cd, Ca}$, moreover among calcium and cadmium apatites, the smallest distortion was observed for hydroxoapatites. Thus, the interaction of the phosphorus ion with the oxygen ion of the hydroxyl group for cadmium and calcium hydroxapatites

is less pronounced compared to the interaction of the phosphorus ion with the fluorine one in calcium and cadmium fluorapatite.

For vanadate calcium apatites, a tendency inverse to the one observed for the calcium phosphate apatites has been found, namely, the electron density on the VO₄ groups increases with decreasing electronegativity of the anion located on the sixth-order axis.

Heavy metal apatites conserve the same tendency for valence band formation as calcium apatite. The sublattice of tetrahedrons as well as for calcium apatites is dominante for forming of the main features of the valence band. The main features in the upper part of the valence band describe the interaction of the metal cation with the oxygen of the PO₄⁻ groups, the interaction of phosphorus with the oxygen inside the PO₄ tetrahedra and the state of the OH-groups.

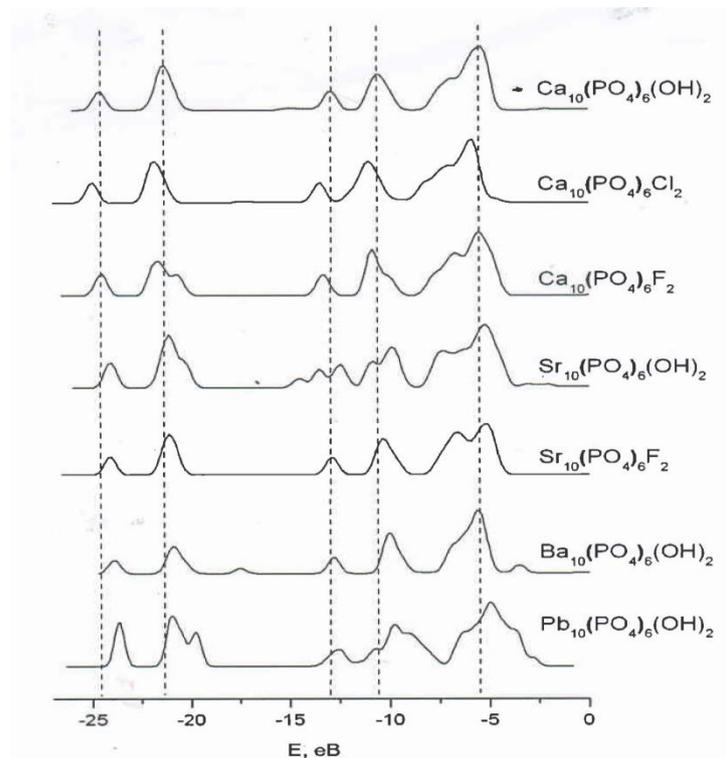


Fig. 7. The total densities of the compounds under study

Isomorphic Ca → Ba substitution leads to an increase in the ionic component of the barium chemical bond with oxygen ions and to a narrowing of

the barium apatite valence band (Fig. 7). The interaction of barium cations with oxygen anions differs significantly for barium in two non-equivalent crystallographic positions. For barium, which is in the second crystallographic position, the degree of ionicity of the chemical bond is significantly higher than it takes place for the barium ions in the first position. As result we can observed a change in the nature of the interaction between metal cation and OH-groups in comparing it wit interaction peculiar to calcium and strontium apatites.

The substitution of $\text{Ca} \rightarrow \text{Pb}$ leads to an increase in covalent component of the chemical bond of lead atoms in the first crystallographic position with oxygen of PO_4 tetrahedra. In the total balance of charge compensation, an increase in the chemical bond ionicity for lead atoms in comparison with calcium apatite was found. However, an increase in the covalent component for lead atoms in the first position leads to a decrease in the degree of chemical bond ionicity in comparison it with the barium apatite chemical bond.

The difference found in the degree of chemical bond covalence for lead atoms that occupy two different crystallographic positions, points out that substitution of calcium by lead is more preferable for calcium situated in the first crystallographic position, which affects the ability to ion exchange between calcium and lead in different positions.

The joint study of the X-ray spectra and the calculated data of calcium and strontium hydroxoapatites demonstrate notable differences in the formation of their energy shells, in particular, revealed a significant increase in the partial contribution of Hs-states to the total state density of Sr-HAP, as well as the shift in 7 eV of the main Hs-density maxima correspondent to Sr-HAP in relation to its counterpart belonging to Ca-HAP. For calcium hydroxoapatite, the band splitting in the region of 15 eV is observed. This effect can be explained as the result of a complex mechanism of hybridization of hydrogen s-density between $\text{Ca}_{(2)} p$ and $\text{Ca}_{(2)} d$ -density through the states $\text{O}_{(4)} p$.

For electron states density curves of fluorapatite atoms in comparison with hydroxoapatite atoms can be observed more wide energy splitting. The reason for this effect reduces to the higher symmetry of fluorapatite tetrahedra compared to hydroxoapatite. As far as strontium hydroxoapatite it manifests a significant widening of infrared band in comparison with fluorapatite, which characterizes the symmetry of the tetrahedra vibration. Also, the strontium fluorapatite F_{2p} -states contribute more than $O_{(4)p}$ -states to the total density of states. Changes of this nature lead to an increase in the bond of metal and fluorine atoms and by this means to the strengthening of the crystalline lattice along the c-axis.

One of the major differences between the electronic structure of barium apatite $Ba_{10}(PO_4)_6(OH)_2$ and calcium apatite resulting from comparison of the calculated state densities for these compounds and the experimental data (Table 4), is the increase of the ionic component of the barium cation chemical bond with oxygen ions belonging to both the PO_4 tetrahedrons and the OH-groups, which indicates an increase in Coulomb interactions in the Ba-HAP crystal and leads to a narrowing of the valence band of barium apatite.

The increase in the ionic component of the chemical bond is also confirmed by the NMR data, according to which the substitution $Ba \rightarrow Ca$ causes the NMR ^{31}P spectrum towards the low frequencies wing by about 2.2 ppm and indicates an increase in the magnetic shielding of phosphorus nuclei, which in this case means an increase in the electron density on phosphorus atoms. It is shown by theoretical calculations that the ionic component of the barium chemical bond in the second crystallographic position with the oxygen of OH- groups is much more pronounced.

Table 4

Electron binding energies(eV) of the core levels of compounds in study
Measurement error is equal to 0.1 eV

Substance	O 1s	P 2p
Ca ₁₀ (PO ₄) ₆ (OH) ₂	531.2	133.9
Ba ₁₀ (PO ₄) ₆ (OH) ₂	530.0	132.2
Pb ₁₀ (PO ₄) ₆ (OH) ₂	530.7	132.9

The reduction of the electron binding energy in oxygen and phosphorus atoms is also observed for the sample of hydroxypyromorphite (Pb₁₀(PO₄)₆(OH)₂), but one notable feature of its electron structure is the possible contribution of electron pair 6s², which shows a low binding energy. Thus, for the Pb²⁺ state, two 6s-electrons can be described as an uncoupled pair, however, depending on the surrounding the unoccupied 6p-orbit suffers hybridization with the 6s-orbit that conducts to formation of a "stereochemically active" no separated pair. Such an electron pair intensely interacts with the O₂valent electrons of the surrounding oxygen and leads to the participation in the chemical bond of lead - oxygen of a previously inactive electron pair. The partial density of lead states obtained by quantum mechanical calculations shows 6s-p-hybridization for lead atoms in the first crystallographic position, whereas for lead atoms in the second crystallographic position, similarly hybridization is significantly less expressed. Because of this fact for the Pb₍₂₎ atoms, covalent component of the chemical bond with the oxygen atoms is slightly less than for the lead atoms in the first crystallographic position. Thus, the reduction of the ionic component of the chemical bond in the complete balance of charge compensation in lead apatites relatively to barium apatites occurs mainly due to lead atoms, which are in the first crystallographic position with a more pronounced covalent chemical bond component.

In the metal sublattice of calcium, barium and lead apatites, indirect interaction between the metal atoms takes place. As it turns out for calcium and

barium apatites, interaction between the metal atoms in the second position by means of oxygen belonged to the hydroxyl group achieves quite tangible values. In lead apatite, a pointed out interaction occurs due to the oxygen belonging to the PO₄-tetrahedron and lead situated in the first crystallographic position.

Summary and conclusions

1. The displacement of the spectral band main maximum which corresponds to the d- and p-states of calcium towards the short-wavelength region has been established. The found effect can be explained as the result of nickel d-states impact due to its lower level of energy localization.
2. Amorphous replacement of calcium atoms by atoms of 3d-metals leads to a decrease in the electron density at the calcium and oxygen atoms. Because of this electron density modification the share of covalent component in the total balance of chemical bond increases.
3. The valence band of calcium phosphate apatites is formed mainly by Ca-3d states.
4. On base of this paper the crystal types of apatite particles texturing can be determined.
5. The anomalous electron density of the part of the valence band formed by P 3p-states has been found.
6. Spatial localization of core electronic 3p-states of calcium is insignificant. As a rule 3p-electrons of calcium are distributed near the correspondent nucleus.
7. High stability of PO₄-tetrahedron at transition from one type of apatite to another is established.
8. Isomorphic substitution $\text{Ca} \rightarrow \text{Ba}$ leads to an increase in the ionic component of the chemical bond of barium with oxygen ions.
9. Substitution $\text{Ca} \rightarrow \text{Pb}$ leads to an increase in the share of covalent chemical bond of lead atoms with oxygen PO₄-tetrahedron.

References

1. Ikeo N., Lijima Y., Niimura N. Handbook of X-ray photoelectron spectroscopy. Tokyo, Japan: JEOL Ltd. 1991. 217 p.
2. Химия радиоэлементов и радиационных превращений в 4-ух томах / под редакцией В.Н. Спицина, В.О. Бахуковой. М.: Наука, 1959. Т. 4.
3. Тарасевич Ю.Н. Строение и химия поверхности слоистых силиконов. К.: Наукова думка. 1988. 248 с.
4. Карбовский В.Л., Загородний Ю.А., Касияненко В.Х. Энергетический ландшафт валентных электронов апатитов природного происхождения // Наносистемы, наноматериалы, нанотехнологии. 2009. Т. 7. №4. С. 990-1010.
5. Карбовский В.Л., Сорока А.П., Шпак А.П., Касияненко В.Х. Квантовомеханические расчеты электронного строения и атомной архитектуры апатитов кадмия и кальция // Доповіді НАН України, 2010. №7. С. 82-86.
6. Шпак А.П. Апатити, Академперіодика. Киев, 2002. 414 с.
7. Загородний Ю.Л., Карбовский В.Л. Электронная структура гидроксопироморфита $Pb_{10}(PO_4)_6(OH)_2$ // Металлофизика и новейший технологии. 2009. Т.31. С.1731-1737.