Functional Materials 17, No.2 (2010)

Electron structure of triple tetrahedral structures on the calcium hydroxyapatite basis

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Received November 12, 2009

The effect of anionic tetrahedral substitution in hydroxyapatite structures on the crystal and electron structure of $Ca_{10}(PO_4)_x(VO_4)_y(AsO_4)_z(OH)_2$, compounds ($x$ = 1, 2, 4; y = 1, 2, 4; z = 1, 2, 4 ($x + y + z = 6$) has been studied. The IR and MAS NMR analyses indicate that progressively the phosphorus substitution by vanadium and arsenic results in increasing lattice parameters that, in turn, is accompanied by changes in distances and by an electron density redistribution in XO_4^{3-} anions. Basing on the XPS and MAS NMR data, it has been established that the distance increase between phosphorus and oxygen results in a substantially increasing ionic component of chemical bond, however, the charge redistribution occurs only between oxygen and appropriate chemical element inside of XO_4^{3-} and does not affect the metal sublattice.

Исследовано влияние анионных тетраэдрических замещений в структуре гидроксиапатита на атомное и электронное строение соединений $Ca_{10}(PO_4)_x(VO_4)_y(AsO_4)_z(OH)_2$, где x = 1, 2, 4; y = 1, 2, 4; z = 1, 2, 4 ($x + y + z = 6$). Метод ЯМР с вращением под магическим углом совместно с ИК спектроскопией показали, что замещение фосфора ванадием и мышьяком приводит к увеличению параметров решетки, что, в свою очередь, сопровождается изменением расстояний и перераспределением электронной плотности в XO_4^{3-} анионах. На основании данных, полученных с помощью рентгеновской фотоэлектронной спектроскопии, а также ЯМР, установлено, что увеличение расстояний между ионами фосфора и кислорода приводит к существенному увеличению ионной составляющей химической связи, причем перераспределение заряда происходит исключительно между ионами кислорода и соответствующим элементом внутри XO_4^{3-} аниона, не затрагивая подрешетку атомов металла.

1. Introduction

Tetrahedral substitution in the apatite structure attract today a considerable interest in the study field of apatite-type systems. As is known [1], the electron structure of hydroxyapatite is mainly determined by the tetrahedral sublattice of PO_4^{3-} anions, where partial isomorphous substitution allows to control purposefully the material properties. In our previous work [2], we have studied the effect of VO_4^{3-} substitution for PO_4^{3-} groups on the electron structure and properties of calcium hydroxyapatite. Calcium hydroxyapatite with a varying degree of substitution of phosphate tetrahedron by the anion of VO_4^{3-} or AsO_4^{3-} was studied in [3–6]. In particular, in [3] the $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ was investigated where x = 0.3, 1.5, 3.0, 4.5, 6.0, in [6] $Ca_5(P_xAs_{1-x}O_4)_3(OH)$ with a wide range of x values was synthesized and studied.

However, presently, of a scientific interest is to study the physical and chemical properties of apatite with PO_4^{3-}, VO_4^{3-} and AsO_4^{3-} simultaneously presented in the tetrahedral sublattice. Therefore, the purpose of this work was to study systematically the effect of anion substitution on atomic and electron structure of the apatite of mixed composition $Ca_{10}(PO_4)_x(VO_4)_y(AsO_4)_z(OH)_2$, where $x = 1, 2, 4$; $y = 1, 2, 4$; $z = 1, 2, 4$ ($x + y + z = 6$), depending on the variation of XO_4^{3-} anions, X = P/V/As, as well as of arsenatapatite ($Ca_{10}(AsO_4)_6(OH)_2$).

2. The research methods

The infrared (IR) spectroscopy, nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy (XPS) were used in this work. To obtain IR spectra, the samples were shaped as tablets. The transmission spectra were recorded in absorption band of XO_4^{3-} anion from 1400 cm^{-1} to 400 cm^{-1} using a "Specord M80" double-beam spectrophotometer (recording range 4000–250 cm^{-1}). The X-ray photoelectron spectra were obtained using a JEOL JSPM-4610 photoelectron spectrometer with a non-monochromatic MgK_α (1253.6 eV) X-ray source. During the experiment, the vacuum in the analytical chamber was 10^{-7} Pa, the accuracy of the electron binding energy was determined to 0.1 eV. The test samples of the arsenatapatite and the mixed composition apatites were prepared as a disperse powder deposited on aluminum substrate. In order to avoid the influence of the charge accumulation on the insulating sample surface during the experiments, a thin gold layer was applied on its surface. The calibration of X-ray photoelectron spectra was carried out against the binding energy of gold Au4f lines, thus providing to obtain a high determination accuracy of electron binding energies for elements of the sample under study. The NMR spectra were recorded on a Bruker Avance 400 spectrometer, at room temperature. The NMR spectra were obtained for both static samples and those being rotated under magic angle (MAS NMR) at 10 kHz and 15 kHz frequencies. The MAS NMR allows to exclude the effects related to the anisotropy and to the dipole-dipole interaction, but does not exclude the second order quadrupole interaction. To take into account the possible effect of a small quadrupole moment of vanadium nuclei on the ^{51}V MAS NMR spectra, the measurements of longitudinal and transverse relaxation times had been carried out for static samples. Magnetic field was referenced against the ^{13}C NMR spectrum of adamantane, which was used as an external standard for magnetic field calibration.

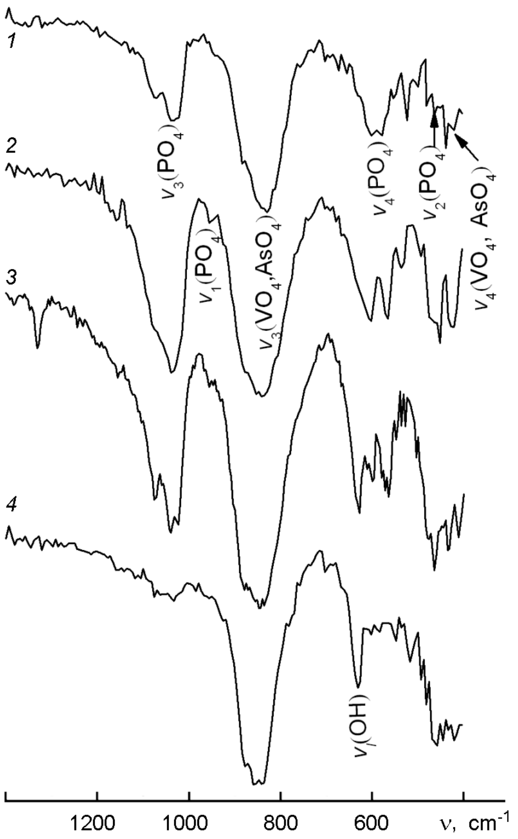

Fig. 1. IR-absorption spectrum of apatites:
1 – $Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$;
2 – $Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$;
3 – $Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$;
4 – $Ca_{10}(AsO_4)_6(OH)_2$.

3. Results and discussion

Fig. 1 shows the IR absorption spectra of the samples in the frequency range of 1400–400 cm^{-1}. Basing on relative intensity changes of the different spectral features with the structure changes of the investigated compounds as well as on the literature data for similar compounds [3–5], it is possible to define unambiguously the positions of various vibrational mode groups for PO_4^{3-}, VO_4^{3-}, AsO_4^{3-} ions. The number of vibrational modes in each group can be thus uses as a basis to determine the symmetry group of XO_4^{3-} ion in the investigated compound. So the free XO_4^{3-} ion has tetrahedral symmetry and belongs to point group T_d. The normal modes of tetrahedral ions are: ν_1, symmetric P–O stretching; ν_2, O–P–O bending; ν_3, P–O stretching, and ν_4, O–P–O bending. For undistorted tetrahedron, the absorptions corresponding to ν_3 and ν_4 vibrational modes can be observed only. The ν_1 and ν_2 vibrational modes become infrared active with a symmetry reduce of XO_4^{3-} anion due to the influence of crystal lattice. Since, in the apatite lattice, PO_4^{3-} ion must have C_s symmetry, the possible point groups for PO_4^{3-}, VO_4^{3-}, AsO_4^{3-} anions in the compound are C_s, C_{2v}, C_{3v}, D_{2d} and T_d [7]. The number of active infrared modes for possible symmetry groups is presented in Table 1.

The absorption bands for apatites of mixed composition corresponding to ~1050 cm^{-1} and ~560 cm^{-1} belong to the ν_3 and ν_4 vibrational modes of PO_4^{3-} ion (Fig. 1). In the range of 944–956 cm^{-1}, the vibrational mode ν_1 is observed for all investigated compounds and is infrared active, that is characteristic only for molecules possessing a dipole moment. The vibration corresponding to ν_2 mode is observed for all the compounds in the range of 452–470 cm^{-1}. The presence of ν_1 and ν_2 modes in all investigated compounds indicates the deformation of XO_4^{3-} tetrahedrons (Table 1), and, therefore, in all studied compounds, XO_4^{3-} ion may have a point symmetry C_s, C_{2v}, C_{3v}, but not higher.

The conventional IR spectroscopy for these compounds does not allow to estimate uniquely the exact number of infrared active modes in each subgroup and, consequently, the symmetry of the ion being investigated. So, the vibrational mode ν_1 for PO_4^{3-} anion is partially overlapped with ν_3 mode for VO_4^{3-} and AsO_4^{3-}-anions, however, a noticeable shift of ν_1 mode to lower frequencies with increasing VO_4^{3-} and AsO_4^{3-} content allows to assume [3] an increase in P–O distances in PO_4^{3-}-anions at increasing VO_4^{3-} and AsO_4^{3-} content. The change of V–O distances in VO_4^{3-}-anion can be revealed using NMR. The shift of isotropic peak in NMR spectra, suggests in general a change of magnetic shielding for nuclei of elements being investigated, that is caused turn by the electron density redistribution between atoms of the compound and indicates the change in the chemical bond nature of. According to Satoshi Hayakawa et al. [8], displacement of isotropic peak and, consequently, changes in electron density near vanadium nuclei is associated with changes in V–O distances of VO_4^{3-} tetrahedrons. So, according to their researches, the decrease of ^{51}V MAS NMR isotropic shift is accompanied by a nearly linear increase in average V–O bond length. In the spectra obtained for these samples (Table 2, Fig. 2c), the isotropic vanadium peak shifts to higher frequencies as the VO_4^{3-} and AsO_4^{3-} content increases, thus it can be suggested that the mentioned content increase results in increasing distance between the vanadium and oxygen atoms. The simultaneous increase of V–O and P–O distances suggests that introduction of large-size VO_4^{3-} and AsO_4^{3-} ions results in an increase of the lattice parameters and, consequently, in increase of P–O distances in PO_4^{3-} tetrahedron. This assumption is confirmed in [3], where an increase of lattice parameters was observed as a consequence of increased VO_4^{3-} anion content. It should be noted that, basing on NMR data, the introduction of smaller size AsO_4^{3-} ions

Table 1. Possible point groups and vibrational modes of PO_4^{3-} ions [7]

Point group	Number of infrared active vibrational modes			
	ν_3	ν_1	ν_4	ν_2
T_d	1	0	1	0
D_{2d}	2	0	2	0
C_{3v}	2	1	2	1
C_{2v}	3	1	3	1
C_s	3	1	3	2

Table 2. Chemical shift δ_{iso} (ppm), half-width $\Delta\delta$ (ppm) of MAS NMR spectrum lines and ^{51}V $\Delta\sigma$-CSA (for static samples)

Compound	^{31}P		^{51}V			^{1}H	
	δ_{iso}	$\Delta\delta$	δ_{iso}	$\Delta\delta$	$\Delta\sigma$-CSA	δiso	$\Delta\delta$
$Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$	4.53	1.52	−606.95	12.48	65	0.68	0.69
$Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$	4.17	1.89	−613.18	14.92	69	0.68	0.69
$Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$	4.03	1.70	−614.20	11.22	68	0.65	0.56
$Ca_{10}(PO_4)_4(VO_4)(AsO_4)(OH)_2$	3.63	1.48	−622.61	16.55	72	0.63	0.61
$Ca_{10}(AsO_4)_6(OH)_2$	–	–	–	–	–	0.71	0.37

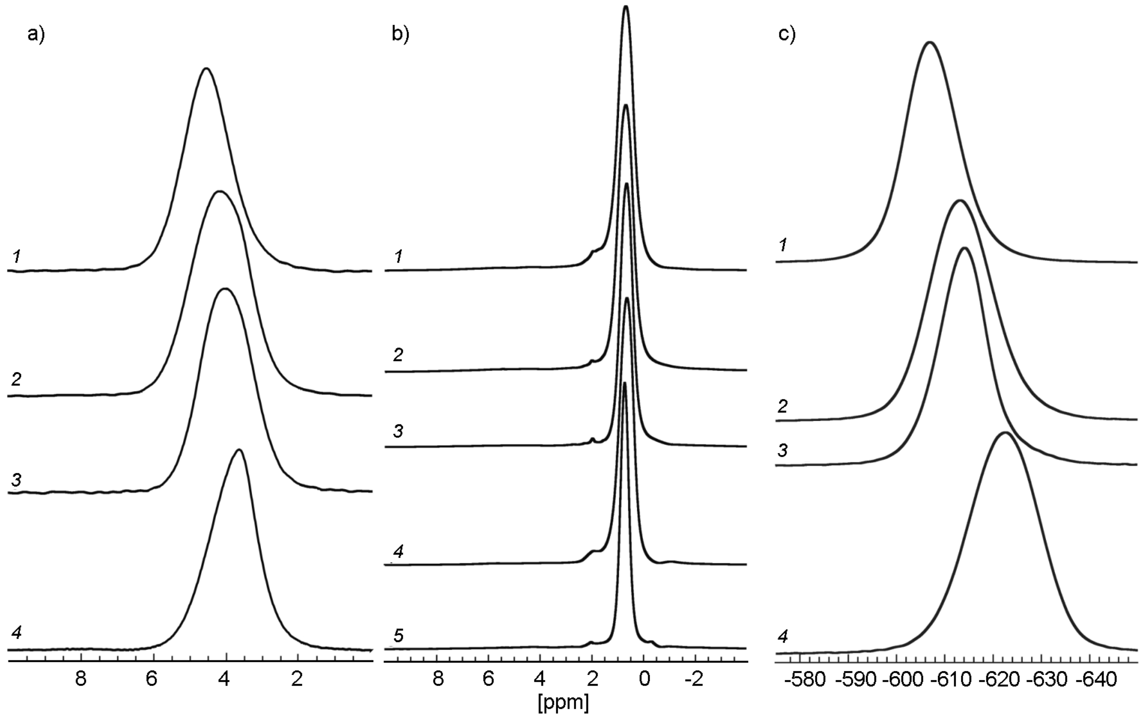

Fig. 2. ^{31}P (a), ^{1}H (b), ^{51}V (c) MAS NMR spectra of compounds: *1*–$Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$; *2* – $Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$; *3* – $Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$; *4* – $Ca_{10}(PO_4)_4(VO_4)(AsO_4)(OH)_2$; *5* – $Ca_{10}(AsO_4)_6(OH)_2$.

causes a smaller increase of V–O and P–O distances in the tetrahedrons and, consequently, to smaller increase in the lattice parameters.

As it follows from the change in the band half-width of ν_3 absorption mode for PO_4^{3-} anions (Fig. 3) and NMR data, the change of lattice parameters is also accompanied by some distortion of XO_4^{3-} tetrahedrons, depending on relative content of ions of the appropriate type. Due to significant overlap of IR absorption spectra of VO_4^{3-} and AsO_4^{3-} tetrahedrons, the ^{51}V NMR spectra obtained for stationary samples (Table 2) were used to determine the degree of VO_4^{3-} tetrahedron distortion. According to these data as well being on the values of ^{51}V MAS NMR isotropic shifts and the Lorentz broadening associated with the spin-spin relaxation time (Table 3) by the relation $1/T_2 = \pi\Delta\nu$, the anisotropy parameters of the chemical shift tensor for vanadium were estimated for each of the samples (Table 2). The small anisotropy size ($\Delta\sigma < 100$ ppm) evidences that vanadium in all samples is in a tetrahedral oxygen environment of Q_0 type and has a nearly spherical symmetry of the chemical shift tensor [9].

The anisotropy parameter in this case is defined by the different shielding of vanadium, depending on the orientation of VO_4^{3-} tetrahedrons with respect to the external magnetic field. Since, according to the XPS (Table 4), the charge on calcium remains unchanged at VO_4^{3-} and AsO_4^{3} replacement for PO_4^{3-}, the differences in vanadium shielding for these substitutions may be explained by changes of V–O distances inside of the VO_4^{3-}-tetrahedron.

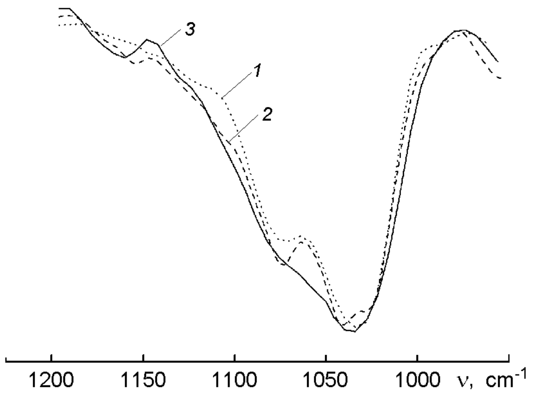

Fig. 3. Intensity-reduced IR absorption spectrum of PO_4^{3-} ions for compounds:

1 – $Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$,
2 – $Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$,
3 – $Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$.

Table 3. The longitudinal (T_1) and transverse (T_2) relaxation of vanadium and phosphorus nuclei of studied compounds

Compound	V	V	P	P
	T_1, s	T_2, μs	T_1, s	T_2, ms
$Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$	3.9	357	31.9	19
$Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$	5.2	539	20.2	18
$Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$	6.1	639	34.1	19
$Ca_{10}(PO_4)_4(VO_4)(AsO_4)(OH)_2$	8.7	697	19.4	17

Table 4. Binding energy (eV) and half-width (in parentheses, eV) for core levels lines of the atoms of studied compounds

Compound	O1s	P2*p*	Ca2*s*	Ca2*p*3/2	Ca2*p*1/2	V2*p*3/2	V2*p*1/2	As3*p*3/2	As3*p*1/2
$Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$	531.0 (2.8)	133.8 (2.2)	439.1 (3.8)	347.4 (2.4)	351.1 (2.2)	517.6 (2.4)	525.4 (3.2)	144.5 (3.1)	149.5 (3.6)
$Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$	531.3 (2.6)	133.5 (2.2)	439.0 (3.8)	347.5 (2.2)	351.1 (2.2)	517.6 (2.2)	525.9 (3.8)	144.3 (3.0)	149.2 (3.4)
$Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$	531.5 (2.2)	133.9 (3.2)	439.1 (4.0)	347.6 (2.4)	351 (2.8)	517.3 (3.0)	524.9 (3.0)	144.3 (3.2)	149.2 (3.8)
$Ca_{10}(PO_4)_4(VO_4)(AsO_4)(OH)_2$	531.4	133.3 (2.4)	439.2 (4.7)	347.6 (2.1)	351.1 (2.5)	517.3	–	144.1 (3.8)	149.4 (4.2)
$Ca_{10}(AsO_4)_6(OH)_2$	531.3 (1.8)	–	439.1 (3.8)	347.4 (2.4)	350.8 (2.4)	–	–	144.2 (3.2)	149.0 (3.2)
$Ca_{10}(PO_4)_6(OH)_2$ [1]	531.2 (2.0)	133.3 (2.4)	439.2	347.3 (2.0)	–	–	–	–	–
$Ca_{10}(VO_4)_6(OH)_2$ [1]	530.1 (2.8)	–	438.7	346.8 (2.1)	350.5	517.0 (1.8)	–	–	–

Thus, it was found that the maximum distortion of VO_4^{3-} tetrahedrons is observed for the compound $Ca_{10}(PO_4)_4(VO_4)(AsO_4)(OH)_2$. A further increase in the substitution degree by vanadium which, as it has been shown in [3], is accompanied by a gradual increase of the lattice parameters, results in a decrease of distortions both in phosphate (Fig. 3) and vanadium tetrahedrons.

The relatively small deformations in XO_4^{3-} tetrahedrons cannot, however, explain the significant changes in the half-width of the MAS NMR spectra. Basing on the spin-spin relaxation values, it is possible to conclude that the half-width of MAS NMR spectral band in this case indicates the presence of close nonequivalent positions of phosphorus and vanadium nuclei in the structures under study. To eliminate the possibility of non-uniform distribution of PO_4^{3-} ions, that could result in interaction between the neighboring anions and thus to broadening of IR absorption bands in one of the samples, thus masking the PO_4^{3-} tetrahedron deformation, the spin-spin relaxation times on ^{31}P nuclei had been measured for $Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$ and $Ca_{10}(PO_4)(VO_4)(AsO_4)_4(OH)_2$ samples containing the same amount of PO_4^{3-} ions (Table 3).

Since the relaxation times for these two samples are practically the same, it is possible to state that the half-width of IR spectra corresponds to the relative distortion degree of PO_4^{3-} ions in the samples. The half-width of NMR spectra cannot be explained by the change in crystallinity degree resulting from such substitutions, as the maximum value for vanadium corresponds to the minimum value for the phosphorus nuclei (Table 2). It seems that such broadening can be explained by the rotation of XO_4^{3-} anions providing them the opportunity to occupy the maximum volume in the structure. Accordingly, different rotation directions and degrees of the tetrahedrons define the set of possible nonequivalent positions of these elements. The presence of VO_4^{3-} and AsO_4^{3-} anions in the $Ca_{10}(PO_4)_2(VO_4)_2(AsO_4)_2(OH)_2$ in equal proportions has the greatest influence on the structure ordering degree. Thus, it is possible to assume that AsO_4^{3-} ions having a smaller size in comparison with VO_4^{3-} ion and occupying an intermediate position in the apatite structure increase the degree of their mutual influence.

According to ^1H MAS NMR spectra (Fig. 2b, Table 2), the structure disordering is accompanied by the change of ^1H chemical shift belonging to OH^- groups, thus demonstrating the change in magnetic shielding of hydrogen nuclei. The minimum magnetic shielding of protons for $Ca_{10}(AsO_4)_6(OH)_2$ increases with replacement of arsenic ions by vanadium and phosphorus, attaining its maximum value for the compound $Ca_{10}(PO_4)(VO_4)_4(AsO_4)(OH)_2$. Due to the fact that, according to the XPS, such substitutions do not influence the metal sublattice (within the measurement accuracy), the change in protons shielding can evidence either a weak charge redistribution between calcium ions and hydroxyl group insufficient for registration by X-ray photoelectron spectroscopy, or the changes in the strength of hydrogen bond $OH\cdots OXO_3$.

The previous studies [3], basing on the displacements of the IR mode matched to OH^- group, indicate an increase in hydrogen bond strength with increasing vanadium content for the $Ca_{10}(PO_4)_{6-x}(VO_4)_x(OH)_2$ ($x = 0.3$, 1.5, 3.0, 4.5, 6.0). An essential overlapping of libration mode of OH^- group, having a value of 632 cm^{-1} for arsenatapatite, with ν_4 belonging to PO_4^{3-} in mixed composition apatites, does not allow to conclude unambiguously its displacement. However, due to the fact that hydrogen bond is usually accompanied by a decrease in magnetic shielding of hydrogen nuclei of OH^- groups [10], for apatites with simultaneous substitution of phosphorus by vanadium and arsenic, increase in magnetic shielding of OH^- group protons, as it follows from ^1H MAS NMR, indicates a strength reduction of $OH\cdots OXO_3$ hydrogen bond with increasing vanadium and arsenic ion content.

The above-described changes in the structure of investigated compounds influence naturally their electron structure. So the XPS data (Table 4) in combination with NMR ones indicate a substantial redistribution of electron density depending on the substitution degree.

The shift of ^{31}P MAS NMR isotropic peak towards higher frequencies (Fig. 2a) and increase in the energy of phosphorus $2p$ core electrons at the increase of both arsenic and vanadium ion content evidences the electron density decrease on phosphorus.

Since the XPS spectrum is the superposition of signals from the entire sample surface of the, the change in binding energy of O1s oxygen core level cannot indicate unequivocally the electron density change on oxygen for a particular type of tetrahedrons. However, taking into consideration the fact that the energy of core electron of calcium is practically the same for all compounds studied, it is possible to assume the charge transfer from phosphorus to oxygen in PO_4^{3-} tetrahedron. Such an electron density redistribution indicates the decrease of initially strongly pronounced covalent component of the phosphorus-oxygen bond in hydroxyapatite. Thus, this substitution type results in a marked increase of ionic component in the P–O chemical bond for substitutions of phosphorus by vanadium and by arsenic, though substitutions by vanadium influence essentially greater the chemical bond ionicity. Increase of VO_4^{3-} ion content results in some increase of the arsenic $3p$ core electron energy that is possibly explained by the increase of lattice parameters and, as in the case of phosphorus, causes some increase in the chemical bond ionicity.

Superpositions of different binding energies in the XPS spectra cause that with increase of VO_4^{3-} anion content the half-width of oxygen O1s core level increases significantly. This seems to be caused by the different ionicity of the oxygen-vanadium bond on the one hand, and oxygen with phosphorus and arsenic on the other one. Thus, the electron density on the oxygen ions depends on the tetrahedron type to which it belongs, and probably it is defined by the fact that, in addition to the maximum ionic radius, vanadium has a significantly different electronic configuration. Participation of more localized $3d$-orbitals of vanadium in the chemical bond results in that as the distance between vanadium and oxygen ions increases, the overlap degree of $3d$ vanadium orbitals with $2p$ oxygen ones is reduced by a much greater extent than the overlap of corresponding phosphorus and arsenic orbitals with oxygen. Perhaps this explains the bond ionicity difference in the tetrahedrons of investigated compounds.

The binding energy of calcium core level electrons is almost the same for all substitution types, hence it follows that the charge redistribution takes place solely between the atoms of an individual anion and does not affect the metal sublattice.

4. Conclusions

The substitution of phosphorus ions by the vanadium and arsenic ones in the structures of mixed composition apatites has been found to increase the lattice parameters and to change the distances within the tetrahedrons. It is shown that an increase of P–O distances in PO_4^{3-} tetrahedron is influenced to much higher degree by the introduction of VO_4^{3-} anions in the structure of investigated compounds, that seems to be explained by large size of VO_4^{3-} anion. It has been noted that such substitutions result in some size change of investigated tetrahedrons, but influence much stronger the spatial topology of tetrahedral sublattice. It has been supposed that hydrogen bond $OH\cdots OXO_3$ strength reduces with increasing vanadium and arsenic content in the mixed composition apatites. It is shown that the charge redistribution in the mixed composition apatites occurs exclusively between sublattices of anions, without affecting the metal sublattice. The electron density redistribution inside of an anion results in an appreciable increase of the P–O chemical bond ionicity in PO_4^{3-} tetrahedron at substitutions of phosphorus both by vanadium and by arsenic, but replacements by vanadium, owing to its electronic structure, have a significantly greater influence on the chemical bond ionicity.

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Електронна будова потрійних тетраедричних структур на основі апатиту кальцію

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Досліджено вплив аніонних тетраедричних заміщень в структурі гідроксиапатиту на атомну та електронну будову сполук $Ca_{10}(PO_4)_x(VO_4)_y(AsO_4)_z(OH)_2$, де x = 1, 2, 4; y = 1, 2, 4; z = 1, 2, 4 ($x + y + z = 6$). Метод ЯМР з обертанням під магічним кутом спільно з ІЧ-спектроскопією показали, що заміщення фосфору ванадієм і миш'яком приводить до зростання параметрів гратки, що в свою чергу супроводжується зміною відстаней і перерозподілом електронної густини в XO_4^{3-}-аніонах. Виходячи з даних, отриманих за допомогою рентгенівської фотоелектронної спектроскопії, а також ЯМР, встановлено, що збільшення відстані між іонами фосфору і кисню приводить до істотного збільшення іонної складової хімічного зв'язку, причому перерозподіл заряду відбувається виключно між іонами кисню і відповідним елементом всередині XO_4^{3-}-аніону, не впливаючи на підгратку атомів металу.