

Electron structure of calcium and cadmium apatites

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Received November 13, 2009

Electron structures of compounds $\text{Me}_{10}(\text{PO}_4)_6\text{X}_2$, where $\text{Me} = \text{Ca}$ or Cd and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{OH}$ were investigated using full potential APW+lo method. The structure and energy location of peculiarities of total and partial densities of states for cadmium apatites were established to be more sensitive to isomorphic substitution of anion fluor for chlor or bromine or OH group than for calcium ones. The $P6_3/m$ space were shown to be preferable for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ than $P6_3$. The dependence of total energy per unit cell on the displacement along c -axis within the limits of space group $P6_3$ for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ was proven to be extremely small that justifies the lability of structure of calcium apatites with respect to this position.

Полнопотенциальным методом ППВ исследовано электронное строение соединений $\text{Me}_{10}(\text{PO}_4)_6\text{X}_2$, где $\text{Me} = \text{Ca}$ или Cd , $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{OH}$. Установлено, что структура и энергетическое положение особенностей полных и парциальных плотностей электронных состояний кадмиевых апатитов значительно чувствительнее к изоморфным замещениям аниона фтора на хлор, бром и гидроксил, в сравнении с кальциевыми апатитами. Показана предпочтительность структуры $P6_3/m$ для $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ и $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ в сравнении с $P6_3$. Для хлоро- и фтороапатитов кальция наблюдалась слабая зависимость суммарной энергии элементарной ячейки от положения аниона в пределах пространственной группы $P6_3$, что подтверждает лабильность структуры апатитов кальция относительно этой позиции.

1. Introduction

Apatite group compounds ($\text{Me}_{10}(\text{ZO}_4)_6\text{X}_2$, where Me^{n+} , $n = 1-3$; Z^{m+} , $m = 1-3$; X^{k-} is an electronegative element) attract attention of scientists for a long time due to a large field of their applications. In particular, they can be used as artificial bioactive compounds compatible with bone tissue, moisture and alcohol sensors, matrices for radioactive waste burial, accumulators of environmentally hazardous substances. Such a variety of physical properties of apatites is due to their capability to iso- and heterovalent substitutions defined by anomalous limits of nonstoichiometry of their composition.

There are numerous studies aimed at electron structure investigations to date, however, a thorough description of isomor-

phism laws can be attained by comparing experimental results with theoretical calculations. Most theoretical electron structure calculations are based on the methods which do not give good agreement with experiment for porous compounds [1-5].

In this work, studied has been the electron structure of $\text{Me}_{10}(\text{PO}_4)_6\text{X}_2$ compounds, where $\text{Me} = \text{Ca}$ or Cd and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{OH}$. The calculations were fulfilled using full potential augmented plane wave method that is most applicable for porous compounds and provides the geometry optimization of atomic positions.

2. Computational procedure

The calculations of total and atom-projected densities of states were performed

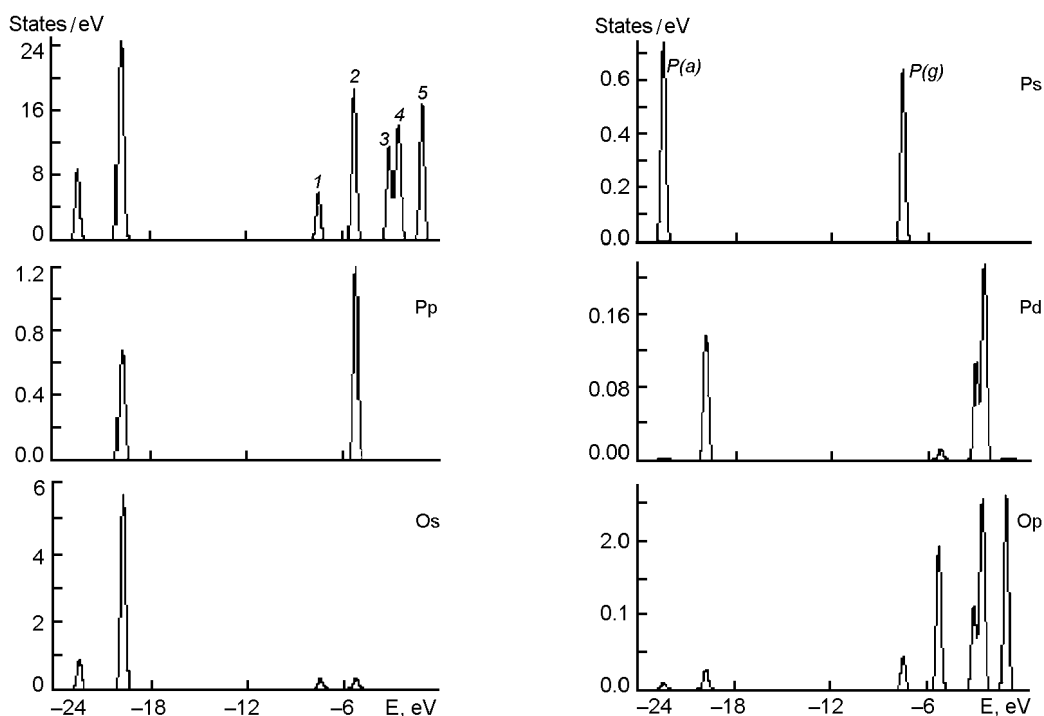


Fig. 1. Total and partial densities of states for isolated PO_4^{3-} tetrahedron.

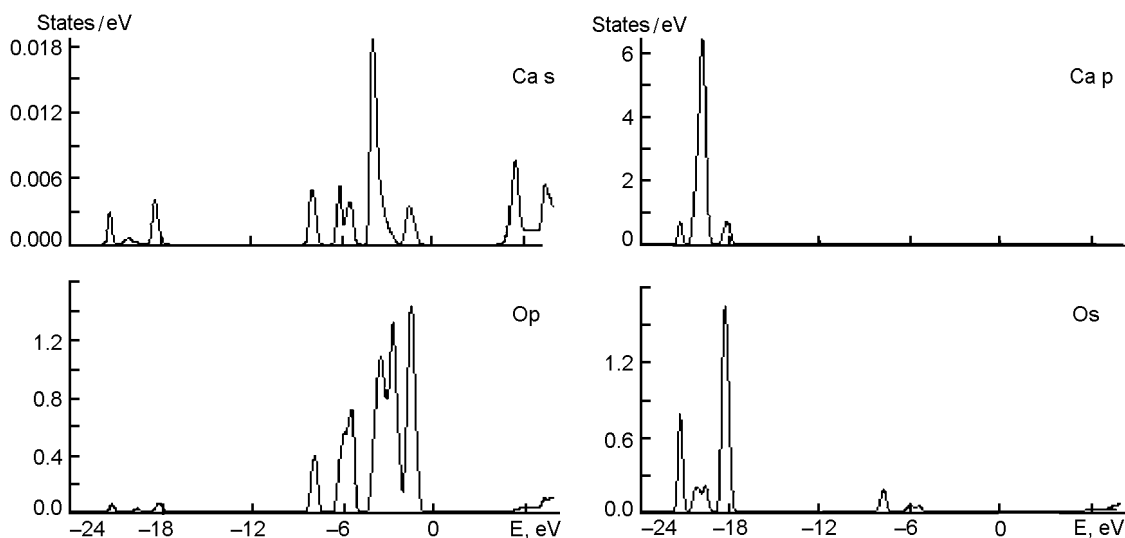
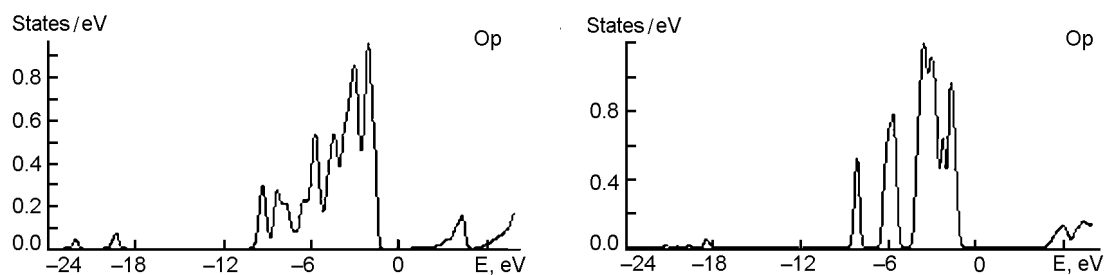
using full potential augmented plane wave method with APW+lo+LO basis set with making allowance for relaxations of atomic positions. Ca 3s, Ca 3p, P 2p were treated as LO. The GGA functional of (PBE) [6] was used for exchange-correlation potential. Integrations over Brillouine zone were accomplished using 2-2-3 \mathbf{k} -point sampling centered at Γ point (4 inequivalent \mathbf{k} -points) [7]. For hydroxyapatites, the 2-1-3 grid was used that corresponds to the same density of \mathbf{k} -points in reciprocal space. $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$, $\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$, $\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$, $\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$, $\text{Cd}_{10}(\text{PO}_4)_6\text{Br}_2$ were considered to belong to $P6_3/m$ space group and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$, to $P2_1/b$ one. The initial atomic positions in the unit cell for geometry optimization was taken from [8]. The unit cell was considered to be cubic with unit cell parameter $a = 16 \text{ \AA}$ in order to calculate molecular levels of isolated PO_4^{3-} anion.

3. Results and discussion

Electron structure of PO_4 -tetrahedra in apatites. Tetrahedral PO_4^{3-} anion is a structure constituent of many crystalline compounds including apatites. As a first approximation, the PO_4^{3-} tetrahedra can be considered as individual molecules with symmetry influenced by lattice force field.

In the free state, the P–O bond length is equal to 1.55 \AA and the point group T_d . To investigate the basic electron structure features of PO_4 complex in apatites, we have calculated the total and partial densities of states for isolated PO_4^{3-} anion and for investigated apatites and the comparative analysis was fulfilled.

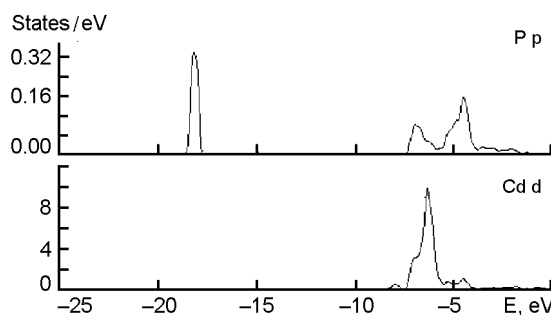
The total and partial densities of states for isolated PO_4^{3-} tetrahedra are shown in Fig. 1. The most substantial contribution to densities of states was observed to be from 2s and 2p states of oxygen. Composition of those partial densities of states defines the shape of total DOS curve. The curve of 2s state of oxygen includes two intense peaks. The first one is located at 19 eV and corresponds to the atomic state. The second is at 22 eV and conforms to hybridization 3s orbital of phosphorus with 2s orbital of oxygen, since P 3s has a singularity at that energy. The O 2p states curve has 5 peculiarities (Fig. 1), the first and the second peaks correspond to hybridization of 2p oxygen states with 3p and 3s states of phosphorus, respectively. The peculiarities 3–4 indicate the hybridization with d states of phosphorus that appeared in PO_4^{3-} anion molecule. The fifth peak corresponds to atomic O 2p state which is a characteristic feature of all the calculated apatites. The same picture was observed for all studied

Fig. 2. Partial density of states for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.Fig. 3. Partial densities of states of O $2p$ for $\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$ (left) and $\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$ (right).

apatites (data are not presented). The electron density on the d orbital of phosphorus for isolated PO_4^{3-} tetrahedron is about 1/4 of $3s$ density while in apatites, this concentration ratio increases and can reach 0.7.

Comparing the O $2s$ states curves for isolated PO_4^{3-} anion and for PO_4^{3-} in calcium apatites, we observed an additional peculiarity of O $2s$ for calcium apatites due to interaction with Ca $3p$ orbital. Thus, analyzing the results of calculations, we can suppose that characteristic feature of investigated calcium apatites is an energy location of Ca $3p$ level in the valence band (Fig. 2). In particular, this fact was established for calcium hydroxyapatites in [4].

The O $2p$ state curve for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ is widened a little with respect to that for isolated molecule (Figs. 1, 2). Considering the shape of oxygen $2p$ states for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, we can conclude that both for $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ and for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ it has 5 peculiarities (data are not presented). These data correlated with those for isolated PO_4^{3-} tetrahedron (Fig. 1). The O $2p$ state curves for $\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$ and $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ contain six peculiarities while for all the calculated cadmium apatites,

Fig. 4. Partial densities of states for $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$.

these curves include more than six peculiarities (Fig. 3).

Along with above-mentioned extra peaks in O $2p$ curves for cadmium apatites, the splitting of P $3p$ peculiarities was established for all the cadmium apatites caused by interaction $3p$ orbital of phosphorus with $4d$ orbital of cadmium ($\text{Cd } 4d \rightarrow \text{O } 2p \rightarrow \text{P } 3p$ hybridization) (Fig. 4).

The relaxations of atomic positions for investigated apatites were performed within the limits of $P6_3/m$ space group, consequently, the point group of PO_4 tetrahedra was C_s . An exception form the hydroxyapatites belonging to $P2_1/b$ space group that

Table 1. P-bond lengths in $(\text{PO}_4)_3$ -tetrahedra obtained by relaxation of atomic arrangement

Compound	P-O(1), Å	P-O(2), Å	P-O(3), Å	P-O(4), Å
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	1.53524	1.54338	1.54338	1.54731
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	1.54952	1.55207	1.55207	1.56431
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	1.55401	1.55848	1.55860	1.55686
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	1.55386	1.54286	1.54286	1.56995
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	1.54601	1.54622	1.54622	1.58148

Table 2. Energy differences between P 3s and O 2s states. (P 3s(a) is P 3s atomic level; (P 3s(g), energy level produced by hybridisation)

Compound	P 3s(a)-O 2s, eV	P 3s(g)-O 2s, eV	P 3p-O 2s, eV
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	-2.966	10.412	12.844
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	-3.033	10.140	12.442
$\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$	-2.802	10.016	12.763
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	-2.885	10.761	12.451
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	-2.748	10.041	13.552
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	-2.023	10.028	12.833
$\text{Cd}_{10}(\text{PO}_4)_6\text{Br}_2$	-3.343	10.401	11.989
$\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$	-2.612	10.386	13.799
Isolated $(\text{PO}_4)^{3-}$ tetrahedron	-2.608	12.234	14.453

Table 3. Energy separations of states for investigated compounds

Compound	O 2p-O 2s, eV	H 1s-O 2s, eV	O 2s(PO_4)-O 2s(OH), eV
$\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$	17.338	14.181	0.51
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	17.387	14.057	0.19
isolated OH^-	18.738	15.089	-

results in the reduction of PO_4^{3-} anion symmetry from C_s point group to C_1 . The results obtained show equal P-O(2) and P-O(3) bond lengths (Table 1) for $\text{Me}_{10}(\text{PO}_4)_6\text{X}_2$ compounds, where Me = Ca or Cd and X = F or Cl, that justifies the attribution of PO_4^{3-} tetrahedron to point group C_s . The difference between P-O(2) and P-O(3) bond lengths indicated that the point group of PO_4 tetrahedra is C_1 .

The nature of P-O bonds in PO_4^{3-} tetrahedron can be considered in the light of changes in energy difference between P 3s and O 2s levels (Table 2) and charge redistribution caused by hybridization. The concentration ratio O s/O p for isolated PO_4^{3-} tetrahedron is larger than those for all the investigated apatites. The energy levels produced by P 3p hybridization with O 2s and P 3s with O 2p were proven to be comparable in their intensities to their atomic levels, that means the covalent character of P-O bonds.

The change of electron densities P 3s, P 3p and O 2s was proven to be more sufficient for cadmium apatites $\text{Cd}_{10}(\text{PO}_4)_6(\text{F, OH, Cl, Br})_2$ than for calcium ones when varying the anion on c-axis (Table 2). Thereby, we can assert the partial electron densities of states P 3s, P 3p and O 2s for cadmium apatites to be more sensitive with respect to isomorphic substitution in anion group than calcium ones.

Electron density of anion located on c axis. The calculated energy difference between 2s and 2p states of oxygen for calcium and cadmium hydroxyapatites are presented in Table 3. The data for isolated ion OH^- are presented for comparison. It has been established that energy difference between O 2p and O 2s levels for cadmium hydroxyapatite is 0.049 eV larger than that for $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$ and H 1s - O 2s is 0.124 eV lower. The energy difference between O 2s(PO_4) and (O 2s(OH)) levels for $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$ is 0.51 eV (Table 3) while

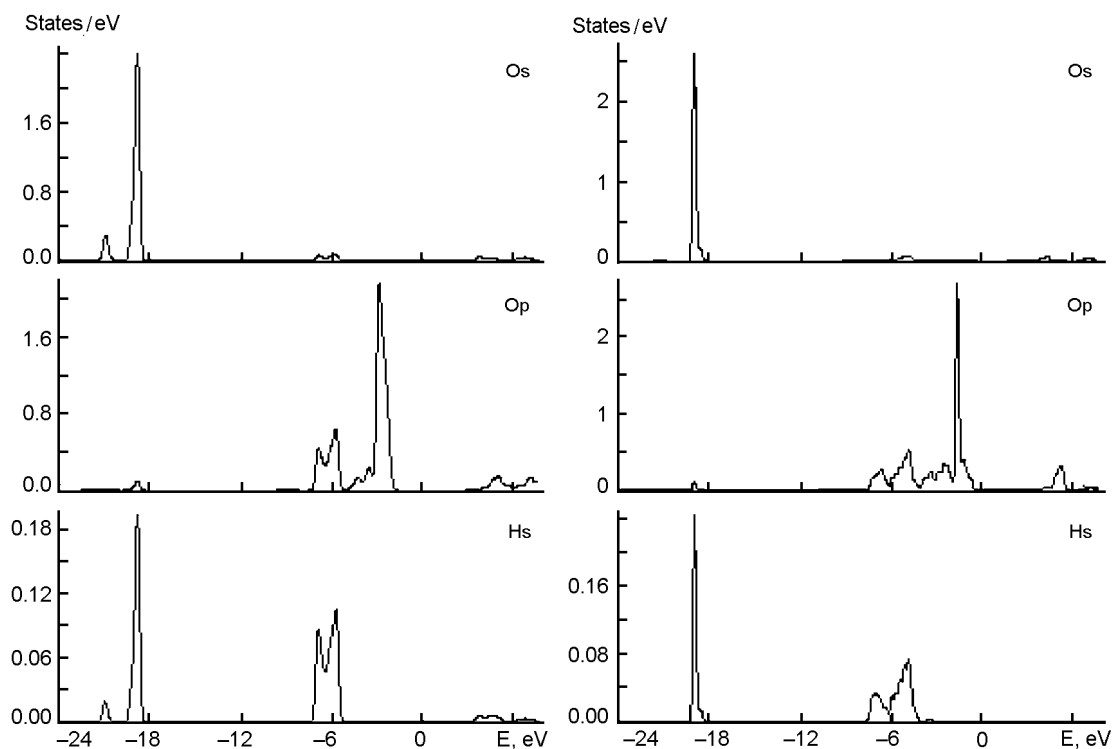


Fig. 5. Partial densities of states for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (left) and $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$ (right).

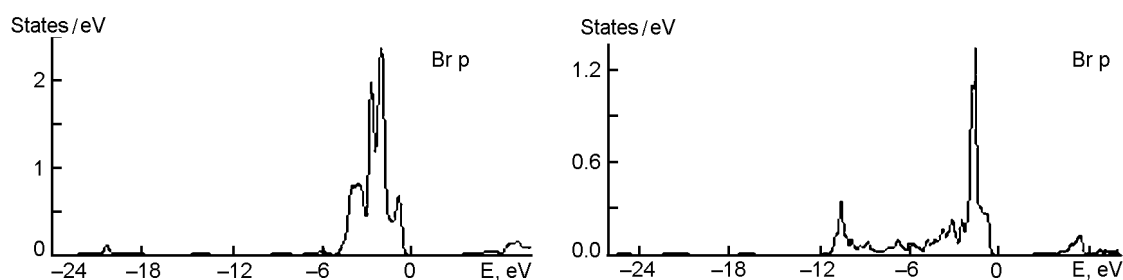


Fig. 6. Partial 4p density of bromine states for $\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$ (left) and $\text{Cd}_{10}(\text{PO}_4)_6\text{Br}_2$ (right).

for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, such shift of O $2s(\text{PO}_4)$ with respect to O $2s(\text{OH})$ is 0.19 eV.

The comparison of partial densities of states for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and $\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$ indicates the difference between charge densities for these compounds (Fig. 5). The curves of 2s states of oxygen and 1s states of hydrogen for calcium hydroxyapatite are observed to have a peculiarity at -20 eV. Such peculiarity was not observed for cadmium apatite; that means the presence of O $2s(\text{PO}_4)$ -O $2s(\text{OH})$ -P 3s interaction for cadmium apatites and absence of such interaction for calcium ones. This is due to the better metallic properties of cadmium than calcium, and thus, the charge outflow from cadmium to oxygen tetrahedra is larger than that for calcium, thus resulting in a stronger interaction

Table 4. Energy distances for investigated apatites

Compound	O $2p$ -O $2s$, eV	X s - O $2s$, eV	X p -O $2s$, eV
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	16.767	-3.537	16.767
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	17.252	-3.021	16.001
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	16.490	3.401	14.068
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	17.088	2.915	14.639
$\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$	15.831	4.735	16.164
$\text{Cd}_{10}(\text{PO}_4)_6\text{Br}_2$	18.828	4.417	17.086

O $2s(\text{PO}_4)$ -O $2s(\text{OH})$ -P 3s for calcium apatites.

The same picture was observed for all the investigated apatites (Fig. 6, Table 4). The presence of Xs - O $2s(\text{PO}_4)$ and Xp - O $2p(\text{PO}_4)$ interactions for calcium apatites has been

Table 5. Band gaps widths for investigated apatites

Compound	Band gap width, eV
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	5.14
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	5.08
$\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$	3.86
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	4.66
$\text{Cd}_{10}(\text{PO}_4)_6\text{F}_2$	2.12
$\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$	2.53
$\text{Cd}_{10}(\text{PO}_4)_6\text{Br}_2$	2.70
$\text{Cd}_{10}(\text{PO}_4)_6(\text{OH})_2$	2.34

established. The interaction $X s - \text{O } 2s(\text{PO}_4)$ for cadmium apatites is appreciably weaker for calcium apatites than for cadmium ones while $X p - \text{O } 2p(\text{PO}_4)$ one is stronger a little. Comparing the shape of $X p$ band for calcium and cadmium apatites, we have found that the latter contains amore pronounced peak corresponding to atomic level and a larger tail (Fig. 6).

The main features of the electron charge density behavior trends have been established (Table 4). The energy separation between $\text{O } 2s$ and $X s$ levels has larger dispersion for cadmium apatites than for calcium ones. On the contrary, the dispersion of $\text{O } 2p - \text{O } 2s$ is larger for calcium apatites. The relatively large difference $\text{O } 2p - \text{O } 2s$ between cadmium bromapatite and calcium bromapatite can be explained by distinction of $\text{O } 2p$ band for $\text{Cd}_{10}(\text{PO}_4)_6\text{Br}_2$. A deviation from the common trend we observed for $X p - \text{O } 2s$ states. The reduction of $X p - \text{O } 2s$ was observed for fluorapatites when calcium was substituting for cadmium. For $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ and for $\text{Ca}_{10}(\text{PO}_4)_6\text{Br}_2$, an increase of this distance was observed.

Total density of states. Comparison of calculation data for the set of $\text{Me}_{10}(\text{PO}_4)_6\text{X}_2$ apatites where $\text{Me} = \text{Ca}$ or Cd and $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{OH}$ (Fig. 7) shows a common feature of filled part of valence band, which has strongly pronounced character with different widths of individual subbands.

Table 6. Lattice constants for investigated compounds

Compound	Calculation					Experiment		
	$a, \text{\AA}$	$c, \text{\AA}$	c/a	V	\AA^3	$a, \text{\AA}$	$c, \text{\AA}$	c/a
$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$	9.72	6.75	0.69	552.29	9.63	6.78	0.70	544.52
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	9.48	6.94	0.73	540.14	9.36	6.88	0.73	522.00

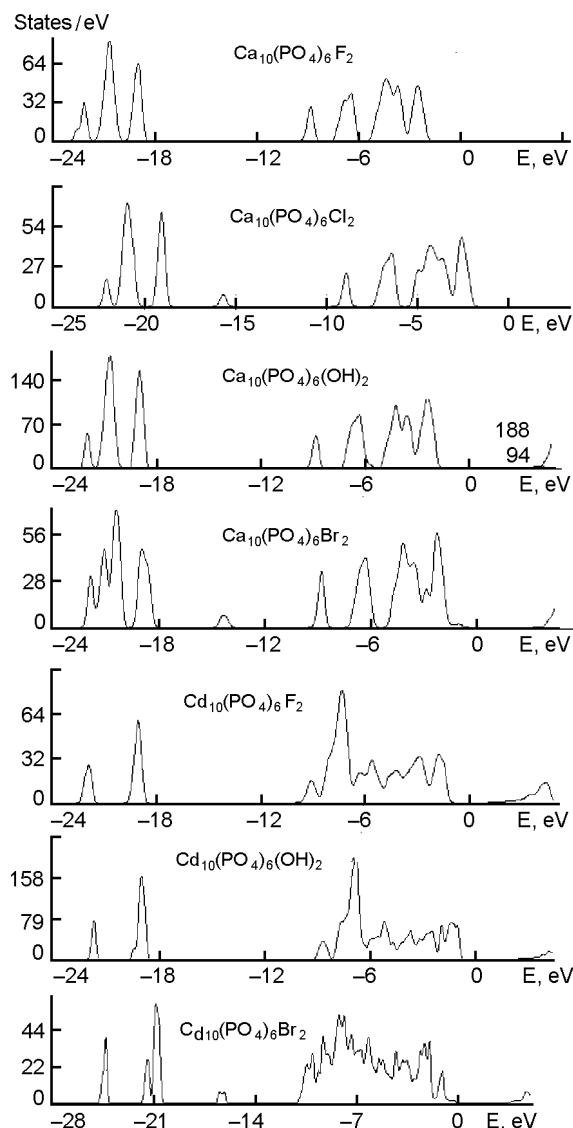


Fig. 7. Total densities of states for investigated compounds.

Two bands separated by energy were found for all the investigated apatites. The upper band is located near "Fermi level" and the lower one is subvalence states. Taking into consideration partial densities of states mentioned above (Figs. 1–3) and the number of individual atomic species, we can conclude that the main contribution to total

densities of states are O 2s and O 2p states of tetrahedral sublattice. Thus, oxygen states of tetrahedral sublattice mainly specify the shape and peculiarities of total density of states curve for all the calculated calcium apatites. A little widening of bands near "Fermi level" was established for cadmium apatites caused by contribution of cadmium 4d states. Some modifications of subvalence bands were observed for calcium and cadmium bromapatites. Those are due to sufficient energy separations of O 2s levels of different nonequivalent oxygen atoms in PO₄ tetrahedra.

Band gaps. In order to describe electron structure of investigated apatites totally, an analysis of band gap widths was performed (Table 5). The analysis of obtained data displayed that band gap widths for calcium apatites are close to experimental values and those for cadmium apatites appeared to be much smaller. This is due to the well-known problem for all calculations of exciting states and band gaps in the framework of density functional theory [9].

The structure calculation of the apatites based on total energy per unit cell. The space group of apatites is specified by anion location on *c*-axis. If the anions have relative coordinates $Z_1 = 0.0$ and $Z_2 = 0.5$ or $Z_1 = 0.25$ and $Z_2 = 0.75$, then the apatite belongs to space group $P6_3/m$. If $Z_1 - Z_2 = 0.5$ and Z_1 is not equal to any above-mentioned value, then the apatite belongs to $P6_3$ space group. Otherwise, the apatite space group is $P2_1/b$. Consequently, chloroapatite, fluoroapatite and bromoapatite can formally belong to any of the above-mentioned space groups and hydroxyapatite, to $P6_3$ or $P2_1/b$. We tried to identify the anion position for Ca₁₀(PO₄)₆F₂ and Ca₁₀(PO₄)₆Cl₂ from energy considerations. Anions were moved within the range of $P6_3$, i.e. the condition $Z_1 - Z_2 = 0.5$ is not breached. The extremely weak dependence of total energy per unit cell is revealed when anions are moved. The total energy amplitude fluctuation is equal to 0.0002 Ry for Ca₁₀(PO₄)₆F₂ and 0.0004 Ry for Ca₁₀(PO₄)₆Cl₂. The minimum of total energy per unit cell in both cases falls on $Z_1 = 0.25$, $Z_2 = 0.75$, thus meaning that the space group $P6_3/m$ is preferable over $P6_3$ for Ca₁₀(PO₄)₆F₂ and Ca₁₀(PO₄)₆Cl₂. However, extremely weak dependence of total energy upon the anion displacement means that anions keep the lability with respect to location on *c*-axis. The larger fluctuation amplitude for Ca₁₀(PO₄)₆Cl₂ than for Ca₁₀(PO₄)₆F₂ can

be explained by lower negativity of chlorine than fluorine.

The lattice constants have been calculated for Ca₁₀(PO₄)₆Cl₂ and Ca₁₀(PO₄)₆F₂ (Table 6). The calculation shows a good agreement with experimental results [10].

4. Conclusions

The energy location of peculiarities in total and partial densities of states for cadmium apatites have been shown to be more sensitive to isomorphic substitution of fluorine anion for chlorine, OH group or bromine than for calcium ones. The interaction $X s - O 2s$, where X is a halogen, was observed for calcium apatites in contrast to cadmium ones because of less charge outflow from Ca to O and X for calcium apatites and therefore, a stronger interaction between O and X. For cadmium apatites, O 2p bands (and therefore total densities of states) are smeared a little with respect to calcium ones due to hybridization Cd 4d - O 2p. The space group $P6_3/m$ has been established to be preferable over $P6_3$ for Ca₁₀(PO₄)₆F₂ and Ca₁₀(PO₄)₆Cl₂. However, extremely weak dependence of total energy upon the anion displacement justifies that anions keep the lability with respect to location on *c*-axis. The calculations using GGA (Perdew, Burke, Ernzerhof) functional gave band gaps for calcium apatites agreeing well with experimental values. The calculations also yielded lattice constants for Ca₁₀(PO₄)₆F₂ and Ca₁₀(PO₄)₆Cl₂ close to the experimental values.

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Електронна структура апатитів кальцію і кадмію

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Повнопотенціальним методом ППХ досліджено електронну структуру сполук $Me_{10}(PO_4)_8X_2$, де $Me = Ca$ та Cd , $X = F, Cl, Br, OH$. Встановлено, що структура та енергетичне положення особливостей повних і парціальних густин станів апатитів кадмію значно чутливіші до ізоморфних заміщень фтора на хлор, бром або гідроксил у порівнянні з апатитами кальцію. Показано пріоритет структури $R\bar{6}_3/m$ для $Ca_{10}(PO_4)_8F_2$ і $Ca_{10}(PO_4)_8Cl_2$ у порівнянні з $R\bar{6}_3$. Для хлоро- і фтороapatитів кальцію спостерігалася слабка залежність сумарної енергії елементарної комірки від положення аніона у межах просторової групи $R\bar{6}_3$, що підтверджує лабільність структури апатитів кальцію відносно цієї позиції.