THE DIRECTED SYNTHESIS OF SORBENTS AND MATRIXES OF A BURIAL PLACE OF RADIOACTIVE AND TOXIC WASTE PRODUCTS

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Introduction

Having a sorption properties, highly dispersed calcium hydroxyapatite allows to remove pollution of wide nature that provides the subsequent long-term storage without secondary pollution [1-3]. However the perspective of such matrixes application as a burial place of radioactive waste products cannot be fully enough covered and proved without revealing interrelation of isomorphic replacements in structure of apatite.

Results and discussion

The changes of electronic structure of calcium apatite due to isomorphic modification by uranium are investigated. Researches were made using both a method of X-ray photoelectronic spectroscopy and quantum-mechanical modelling in LMTO approximation.

At isomorphic replacement of calcium with uranium in calcium hydroxyapatite (Ca-HAP) all atoms undergo changes in energy electron bonding. Line O 1s of oxygen increases the energy electron bonding on 1.0 eV at preservation of line width. Core electrons lines of calcium are shifted aside of bigger bonding energy so for Ca 2s-level shift is 1.1 eV; Ca 2p lines - 1.0 eV. The 2p line of phosphorus electrons is displaced aside bigger energy on 1.0 eV in this case also. Hence, at isomorphic modification of Ca-HAP by uranium there are appreciable changes in electronic structure of Ca-HAP components, and, the greater shift is observed at the electronic levels located closer to the valent zone [4].

The bonding energy of uranium atom 4f electrons is close to one in UO_3 compound [3] that means they have maximum valency for uranium atoms. However, for uranium-containing apatite shift of 4f electrons bonding energy is greatly larger that for UO_3, at the same time, symbasisical changing of spectrum line width is observed that means the effect of small amount of substance or clustered effect takes a place.

In accordance with quantum-mechanical calculations energy states of oxygen define the form of FDS (full density of states) curve of $Ca_9U(PO4)_6(OH)_2$, as well as in case of Ca-HAP [5]. At transition to uraniferous apatite displacement of all peaks of electronic states density of $O_{(1)}$ s, $O_{(1)}$ p and $P_{(1)}$ s, $P_{(1)}$ p aside low energies is observed, that can be evidence of increasing of bonding energy of P-O in a tetrahedron. Bonding energy of $O_{(2)}$ s and $P_{(2)}$ p electrons lightly increase at simultaneous reduction of bonding energy of $O_{(2)}$ p and $P_{(2)}$ s, that means the redistribution of electronic density for a case of sp^3-hybridization. Densities peaks of $O_{(3)}$ p and $O_{(4)}$ p become more expressive in the region of 7-8 eV. All this testifies to decrease of symmetry of tetrahedron PO_4.

It is necessary to note, that for all electronic density of calcium there is 0.7 eV peak shift to the low bonding energies in the region of 10 eV. If one takes into account that $P_{(1)}$ p, $P_{(2)}$ p и $O_{(1)}$ s, $O_{(1)}$ p, $O_{(2)}$ s, $O_{(2)}$ p, $O_{(3)}$ s, $O_{(3)}$ p have the same shifts, loosening of Ca-O-P bonding is clear.

The isomorphic impurity of uranium essentially influences the form of FSD curve of stochiometric Ca-HAP. Because of difference of calcium and uranium radiuses reduces the tetrahedron symmetry under uranium occurrence in Ca-HAP lattice, there is a split and shift of available peaks and appearance of new one. Thus for $Ca_{(1)}$ s, $Ca_{(1)}$ p, $Ca_{(1)}$ d и $Ca_{(3)}$ d-electronic densities peak spitted on 3 in the region of 5-8 eV, and $Ca_{(3)}$ s, $Ca_{(3)}$ p on 2. New peak appears on $Ca_{(1)}$ p and $Ca_{(3)}$ p curves near to 8 eV. Main peak of $Ca_{(2)}$ s-electronic densities shifts on 1.5 eV, converges and its intensity grows a little. Form of this peak correlates with form of corresponding peak for Us-density. For $Ca_{(3)}$ s and $Ca_{(3)}$ d-densities также peak appears on 8 eV also, splitting of peak on 6 eV on 2 pats takes place. Essential changes of densities of electronic states observed for $O_{(5)}$ p and $O_{(6)}$ p. Peak appears on 7 eV. The peak intensity rises in the region of 10 eV. 2 peaks become more significant in the area of 20-25 eV that can be because of interaction of hydroxyl group oxygen with uranium. Peak shifting on 2 eV to the region of high energies is observed for $O_{(7)}$ s, $O_{(7)}$ p и $O_{(8)}$ s, $O_{(8)}$ p state densities. The same shifts take place for $H_{(1)}$ s и $H_{(2)}$ s. Peak form for hydrogen in the area of 15-17 eV is similar to corresponding form of $O_{(7)}$ p and $O_{(8)}$ p peaks, that is a result of reflection of O-H bonding.

Correlation of displacement of X-ray photoelectron line positions and the computation data (the atom of uranium is located in $Ca_{(2)}$ positions) is evidence of a preferable location of uranium in $Ca_{(2)}$ positions (fig. 1).

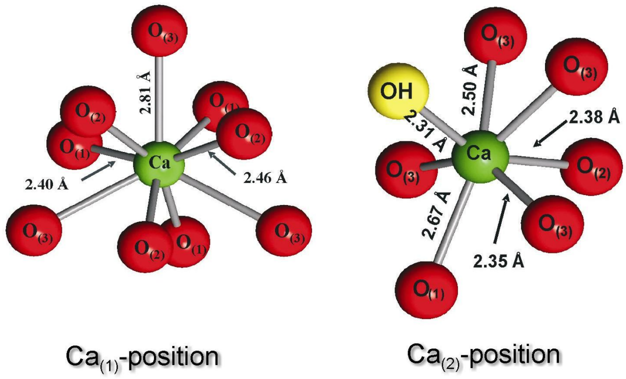

Fig. 1. Position of uranium in hydroxyapatite at isomorphic replacement of calcium.

Conclusions

Isomorphic replacement of calcium hydroxyapatite by uranium results in decreasing of tetrahedrons PO_4 symmetry and increasing of Ca-O-P bonding.

Observable change of 4f electron line width of uranium is determined by effect of the small contents of the alloying additive or cluster effect.

Comparison of spectral and quantum-mechanical data allowed to conclude, that atoms of uranium occupy preferable in $Ca_{(2)}$ positions in the structure of hydroxyapatite. This fact makes the perspective for controlled creation of matrixes for a long-term burial place of radioactive waste products and others toxic materials.

References

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