UDC 546.185

STRUCTURES OF NEW TRIPLE PHOSPHATES $Ca_9CoM(PO_4)_7$ (M - Li, Na, K).

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New triple phosphates $Ca_9CoM(PO_4)_7$ (M=Li, Na, K) were synthesized by solid state method. Their crystal structures were determined by Rietveld analysis. They are related to tricalcium phosphate and crystallize into trigonal system (space group R3c) with unit-cell parameters a=10.327(1) Å, c=37.10(1) Å, M=Li; a=10.351(1) Å, c=37.073(1) Å, M =Na; a=10.401(1) Å, c=37.009(1) Å, M=K. Five independent cation sites are filled in $Ca_9CoM(PO_4)_7$ (M=Li, Na, K). Cobalt occupies the octahedral site M(5), alkali metal cations occupy the M(4).

Introduction. The features of the crystal structures of β-$Ca_3(PO_4)_2$ [1] give the possibility for iso- and heterovalent substitutions of Ca^{2+} by M^+, Me^{2+}, R^{3+}, and R^{4+} cations [2]. These substitutions lead to the formation of the solid solutions on the base of the β-$Ca_3(PO_4)_2$ structure. The solid solutions of $Ca_{3-x}Me_x(PO_4)_2$ (Me=Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sr, Pb, Ba) were studied by Nord. The schemes of heterovalent substitutions are described in details by [2]. Among the triple phosphates with the structure of β-$Ca_3(PO_4)_2$ crystal structures were studied only for $Ca_9MgM(PO_4)_7$ (M=Li, Na, K) and $Ca_{18}Na_3Fe(PO_4)_{14}$.

The whitlockite-like compounds with cobalt cations are of great interest because of their catalytic properties [3]. In this paper we describe the synthesis and crystal structures of the new triple phosphates $Ca_9CoM(PO_4)_7$ (M=Li, Na, K).

Synthesis. The phosphates $Ca_9CoM(PO_4)_7$ (M=Li, Na, K) were synthesized by solid state reactions from stoichiometric mixtures of $Ca_2P_2O_7$, $CaCO_3$, Co_3O_4, and corresponding carbonates M_2CO_3 (M=Li, Na, K) at 1273 K for 50-90 h in air. The compounds obtained were light violet in color and single phase. The indexing of the powder diffraction patterns of $Ca_9CoM(PO_4)_7$ (M=Li, Na, K) has been submitted to the Powder Diffraction Files. The corresponding unit-cell parameters of merit are a=10.3275(1) Å c=37.103(1) Å, F_{30} = 161.1, M=Li; a=10.3514(1) Å, c=37.073(1) Å, F_{30} = 142.6, M = Na; a = 10.4015(1) Å, c=37.012(1) Å, F_{30} = 210.8, M=K.

Structure Determination. Powder diffraction data for structure determination were obtained at room temperature in Bragg-Brentano geometry using a Siemens D500 powder diffractometer equipped with a primary SiO_2 monochromator (Cu Ka1 radiation, X. = 1.54060 Å) and a position sensitive detector (Braun). The data were collected over the range 10–110° 20 with a step Δ(2θ) = 0.01°. Effective counting time was 30 min per step.

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The crystal structures were refined by the Rietveld method using the program RIETAN-97 [4]. Scattering factors for Ca^{2+}, Co^{2+}, Li+, Na+, K+, P, and O^{2-} were used. The background was refined with a fifth-order polynomial. The peak profile was refined by a modified pseudo-Voigt function.

The atomic coordinates of $Ca_{9,5}Co(PO_4)_7$ were used as starting parameters for structure refinements. The cobalt cations were placed in the M(5) site as in $Ca_{9,5}Me(PO_4)_7$ (Me=Co, Cu). Alkali metal cations were placed in the M(4) site as it was obtained for $Ca_9MgM(PO_4)_7$, $Ca_{10}M(PO_4)_7$ (M= Li, Na, K), and $Ca_{10}K(VO_4)_7$. The structure refinements in these models gave a good agreement between the observed and calculated patterns and reasonable values of isotropic thermal atomic parameters for all cations. Final plots of observed electron density maps did not show residual peaks. The electron density on different electron density maps did not exceed ±0.8 e/$Å_3$.

Results and discussion. The structures of $Ca_9CoM(PO_4)_7$ (M=Li, Na, K) can be described as the structure of $Ca_{9.5}Co(PO_4)_7$ with replacement of (Ca2+ + □) (□=vacancy) by 2M+ in the M(4) site. In its turn, the structure of $Ca_{9.5}Co(PO_4)_7$ can be described as the structure of β-$Ca_3(PO_4)_2$ [1] with replacement of Ca^{2+} by Co^{2+} in the octahedral site M(5). Most of the Ca(l)-O, Ca(2)-O, and Ca(3)-O cation to oxygen bond lengths are the same, within experimental error, for $Ca_9CoM(PO_4)_7$ (M=Li, Na, K) and β-$Ca_3(PO_4)_2$ [1]. The differences in cation to oxygen bond lengths are observed for the M(4) and M(5) sites. The octahedrons $Co(5)O_6$ in $Ca_9CoM(PO_4)_7$ (M=Li, Na, K) are very close to each other, but they are more distorted than in β-$Ca_3(PO_4)_2$ (d(Ca(5)-O(24))=2.238(4) Å or d(Ca(5)-O(33))=2.287(4) Å).

The M(4) site in (β-$Ca_3(PO_4)_2$ is an extended cavity along the c axis (threefold axis) and can be described as $M(4)O_{15}$: $O_3(12)O_3(21)O_3(22)O_3(23)O_3(33)$ (Fig. 1). Li+ cations in $Ca_9CoLi(PO_4)_7$ are located below the plane formed by the O(21) atoms (zLi=0.164(2), zO(21)=0.1752(3)). The distance of Li-O(22)=2.94(3) Å (*3) is longer than the usually observed distances of Li-O (2.00(6)-2.41(6) Å) in other compounds. Three distances of Li-O(21) = 2.35(1) Å are also longer than the ion radius sum of rVI(Li+) + r(O^{2-})=2.14 Å. Thus, Li+ cations are weakly bonded to oxygen atoms and actually have a coordination number (C.N.) of 3. The refinement with displacing of Li+ from (0,0,z) to (x,y,z) gave x and y equal to 0 within experimental error. An attempt to split the Li+ cations into two positions (0, 0, Z_1) and (0,0, Z_2) as it has been done for $Ca_9MgLi(PO_4)_7$ [4] was unsuccessful. Na+ and K+ cations in $Ca_9CoM(PO_4)_7$ (M=Na, K) and Ca^{2+} cations in $Ca_{9.5}Co(PO_4)7$ and β-$Ca_3(PO_4)_2$ are located above the plane formed by the 0(21) atoms. The distances of K-O(12)=3.04(1) Å and K-O(22)=3.21(1) Å in $Ca_9CoK(PO_4)_7$ differ less than the corresponding distances of Na-O (2.92(1), 3.36(1) Å) in $Ca_9CoNa(PO_4)_7$ and Ca-O (2.90(6), 3.39(6) Å) in $Ca_{9.5}Co(P0_4)_7$. The coordination number of K^+ can be considered equal to 9. Unambiguous choice of coordination numbers for Na^+, Ca^{2+} (in $Ca_{9.5}Co(PO_4)_7$), and especially Li^+ is difficult.

Similar behavior of unit-cell parameters is observed for series $Ca_9MgM(PO_4)_7$ (M=Li, Na, K [4], 0.5(Ca + □)) and $Ca_{10}M(PO_4)_7$ (M=Li, Na, K, 0.5(Ca + □). The a parameters for compounds with M(4)=0.5(Ca + □) are almost the same as for M=Na, while the c parameters for M(4)=0.5(Ca + □) are greater than for M =Na. The a parameter and unit-cell volume increase and the c parameter decreases in the series Li-Na-K for compounds $Ca_9MeM(PO_4)_7$ (Me=Co, Mg [4], Ca; M = Li, Na, K). The c parameter for $Ca_{l0}K(VO_4)_7$ (c=37.860) is also less than for $Ca_3(VO_4)_2$ (c=38.028). Such unexpected changes of unit-cell parameters can be explained in the following manner. In $Ca_9CoM(PO_4)_7$

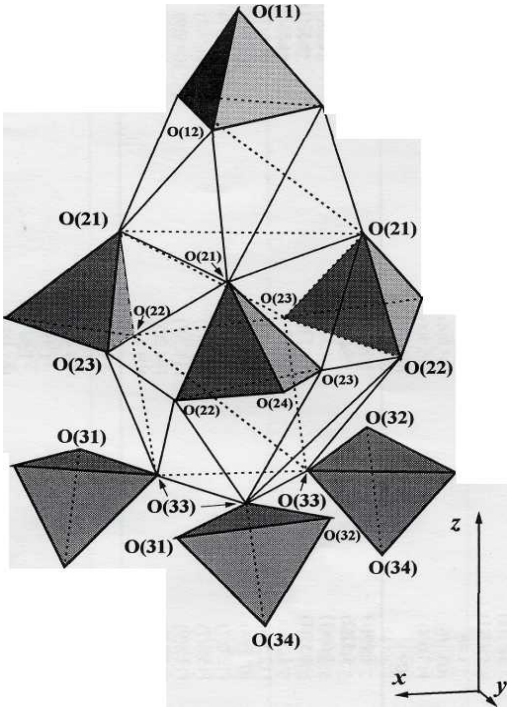

Fig. The cavity of $M(4)O_{15}$ and the surrounding PO_4^{3-} groups

(M=Li, Na, K) and other compounds with the increase of M+ cation radius, alkali-metal cations tend to force apart the $M(4)O_{15}$ cavity along the a and b axes. This leads to the increase of the a parameter. Note that the distance K-O(21)=2.55(1) Å is less than the sum of ionic radii of K+ and O^2-r_{IX} (K+) + $r(O^{2-})$=2.95 Å and also less than usually observed K-O distances 2.65(5)-3.21(5) Å for C.N.=9. The coordination number for Na+ and especially K+ tends to increase. This leads to the shrinkage of the $M(4)O_{15}$ cavity along the c axis and the decrease of the c parameter. The distances O(21)-O(21) in the cavity $M(4)O_{15}$ are equal to 4.02, 4.06, and 4.39 Å for M = Li, Na, and K, respectively. Cations with radius 0.92, 0.94, and 1.14 Å can freely pass through the plane formed by three oxygen atoms O(21) for M=Li, Na, and K, respectively. Thus, Li+ cations (r_{VI} = 0.74 Å) can move inside the $M(4)O_{15}$ cavity, where is Na+ (r_{VI} = 1.02 Å) and K+ (r_{IX} = 1.55 Å) cations are fixed in the upper part of the $M(4)O_{15}$ cavity (Fig.).

References

1. Dickens, B., Schroeder, L.W., Brown, W.E. (1994). The structures of phosphates. Journal Solid State Chemistry,10, 232–240.
2. Lazoryak, B.I. (2006). Synthesis of geterovalency. Russian Chemical Reviews, 65, 287.
3. Nord, A.G., Miner, N.J. (1983). The structure of $Ca_{3-x}Me_x(PO_4)_2$. Chemistry,11, 489.
4. Sheldrick, G.M. RIETAN-97. (1997). A program for crystal structure refinement. Release 97-2. University of Göttingend, Germany.

АНОТАЦІЯ

Лаврик Р.В. Орехова Д.Д. *Структура нових триполіфосфатів $Ca_9CoM(PO_4)_7$ (M –Li, Na, K) // Біоресурси і природокористування. – 2016. – **8**, №3–4. – С. 40–42.*

Стаття присвячена синтезу нових триполіфосатів $Ca_9CoM(PO_4)_7$ (M = Li, Na, K) твердофазним способом. Кристалічні структури нових сполук були встановлені методом РСА і мають такі параметри: a = 10.3276(1) Å, c = 37.100(1) Å, M = Li; a = 10.3515(1) Å, c = 37.073(1) Å, M = Na; a = 10.4017(1) Å, c = 37.009(1) Å, M = K.

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Статья посвящена синтезу новых триполифосфатов $Ca_9CoM(PO_4)_7$ (M = Li, Na, K) твердофазным методом. Кристаллические структуры новых соединений были установлены методом РСА и имеют такие параметры: a = 10.3276(1) Å, c = 37.100(1) Å, M = Li; a = 10.3515(1) Å, c = 37.073(1) Å, M = Na; a = 10.4017(1) Å, c = 37.009(1) Å, M = K.