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

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The progress of inorganic chemistry is syntheses of 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* = 10.3276(1) E, *c* = 37.100(1) E, M = Li; a = 10.3515(1) E, c = 37.073(1) E, M = Na; *a* = 10.4017(1) E, *c* = 37.009(1) E, M = K. All 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) Site. The features of the crystal structures of β-$Ca_3(PO_4)_2$ give the possibility for iso- and heterovalent substitutions of Ca^{2+} by M^+, Me^{2+}, R^{3+}, and R^{4+} cations. 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. 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 main idea of this work is syntheses phosphates. 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 and figures of merit are *a* = 10.3275(1) E *c*= 37.103(1) E, F_{30} = 161.1 (0.0058, 32), M = Li; *a* = 10.3514(1) E, *c* = 37.073(1) E, F_{30} = 142.6 (0.0062, 34), M = Na; *a* = 10.4015(1) E, c = 37.012(1) E, F_{30} = 210.8 (0.0038, 37), M = K.

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/E^3. The details of data collection and refinement are given. The final atomic parameters are listed, presents selected interatomic distances and angles.