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First row transition metal phosphates: novel structure types, morphotropic and homologous series, topological correlations

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First row transition metal phosphates (-$Mn_3(PO_4)_2$, $Na_{1.265}Mn^{2+}_{2.690}Mn^{3+}_{0.785}(PO_4)_3$, $KFePO_4$ and $Cs_2Ti(VO_2)_3(PO_4)_3$, have been obtained under hydrothermal conditions. Their crystal structures were determined by single crystal X-ray diffraction (IPDS-II area detector system (Stoe), MoK_α, R = 0.019, 0.028, 0.023, 0.030). Three phases from four under consideration have novel structure types.
λ-$Mn_3(PO_4)_2$ is a new (third) modification of Mn^{II} orthophosphate having monoclinic symmetry (sp. gr. $P2_1/c$) like the α and β' phases. The relations of its new structure type to the other polymorphs and derivative Mn and Fe phosphates are discussed.
$Na_{1.265}Mn^{2+}_{2.690}Mn^{3+}_{0.785}(PO_4)_3$, a new - and the first synthetic - member in the wyllieite mineral group, contains Mn^{3+} cations in the position usually occupied by Al (or Fe^{3+}).
In $KFePO_4$, [FeO_4], [FeO_5] and [PO_4] oxo-complexes form a microporous 3D para-framework with open channels along the *a* and *b* directions. The structural relations within the morphotropic series of non-isotypic K*M*PO_4 compounds (*M* = Zn, Ni, Mn, Fe) are discussed.
The first structurally confirmed titanium vanadyl(V) phosphate $Cs_2Ti(VO_2)_3(PO_4)_3$ is formed by [VO_5], [PO_4] and [TiO_6] polyhedra sharing vertices. An anionic framework with intersecting channels in the [001], [100], [010] and [110] directions, containing the Cs cations, suggests considering the new compound as a possible 3D ion-conductor. Topological relations between this new structure and that of mineral benitoit $BaTiSi_3O_9$ are discussed.

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Symmetry in the Crystal Growth Processes from the Melt

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The conception is based on the symmetry-thermodynamic method of analyzing the interaction forces and flows in the systems of crystal growth from the melt. The following interrelations are studied: scalar - axial vector - polar tensor of even rank; pseudoscalar - polar vector - pseudotensor of even rank - polar tensor of odd rank. The method of the crystal growth analysis includes (a) determination of the thermodynamical forces and flows in the system, (b) determination of the tensor ranks and types (and Curie symmetry groups of flows and forces), (c) theoretical and experimental determination of the values of forces and flows and their comparison. The experimental part of the work included germanium and tellurium dioxide single crystals growth from the melt. Asymmetrical gradient annealing was applied to improve the optical characteristicse of the crystals. Large germanium (with a diameter more than 600 mm) and tellurium dioxide (with a mass exceeding 2 kg) single crystals with minimal dislocation densities were obtained.