

MS13- New insights on diffraction studies of minerals and related materials

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Crystal chemical features in the row of phosphates and vanadates with alkaline and transition metals

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New crystals were synthesized under hydrothermal conditions, simulating natural middle-temperature hydrothermal zones ($T = 230\text{--}280\text{ }^{\circ}\text{C}$; $P = 70\text{--}100\text{ atm}$) using complex vanadate/phosphate systems with transition $M = \text{Mn, Co, Ni, Cu}$ and alkaline cations $A = \text{Na, K, Rb, or NH}_4$, and Cl^- , F^- , CO_3^{2-} mineralizers. The X-ray spectral analysis (JEOL SEM with EDS) provided the chemical composition of the crystals. The crystal structures were determined by single-crystal X-ray diffraction (XCalibur-S-CCD diffractometer). Most of new compounds were found out to be new synthetic modifications of minerals alluaudite $\text{KCuMn}_3(\text{VO}_4)_3$, niahite $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$, mahnertite $\text{K}_{2.5}\text{Cu}_5\text{Cl}(\text{PO}_4)_4(\text{OH})_{0.5}(\text{VO}_2) \cdot \text{H}_2\text{O}$, phosphoellenbergerite $\text{Na}_{0.91}\text{Co}_6[\text{HPO}_4][\text{H}_{0.36}\text{PO}_4](\text{OH})_3$, elpasolite $\text{Rb}_2\text{NaAlF}_6$, and $(\text{NH}_4)_2[(\text{V,P})_2\text{O}_6]$ with pyroxene structure type; others are «mineralogically probable» phosphates $\text{RbCuAl}(\text{PO}_4)_2$, $\text{Na}_2\text{Ni}_3(\text{OH})_2(\text{PO}_4)_2$, $\text{Rb}_2\text{Mn}_3(\text{H}_2\text{O})_2[\text{P}_2\text{O}_7]_2$, $(\text{Al,V})_4(\text{P}_4\text{O}_{12})_3$.

In accordance with Sandomirsky-Belov principles [1], applied to classification of phosphates with amphoteric oxo-complexes [2], the crystal chemical function of amphoteric metal atoms in all new structures was revealed [3]. In five crystal structures the octahedral complexes of amphoteric metals in the lowest oxidation state build the cationic part of the structure, forming structure fragments of different dimensionality. These are isolated 0D $(\text{Al,V})\text{O}_6$ polyhedra in tetraphosphate $(\text{Al,V})_4(\text{P}_4\text{O}_{12})_3$, 1D columns of MnO_6 octahedra in diphosphate $\text{Rb}_2\text{Mn}_3(\text{H}_2\text{O})_2[\text{P}_2\text{O}_7]_2$, 2D layers of MnO_6 , or NiO_6 octahedra in new polymorphic modification of niahite $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{Ni}_3(\text{OH})_2(\text{PO}_4)_2$, respectively, and 3D framework of CoO_6 octahedra in synthetic phosphoellenbergerite $\text{Na}_{0.91}\text{Co}_6[\text{HPO}_4][\text{H}_{0.36}\text{PO}_4](\text{OH})_3$.

In the compounds containing several types of amphoteric metals, its coordination environment and crystal chemical function depends on electronegativity. Thus, in the $\text{RbCu}[\text{Al}(\text{PO}_4)_2]$ structure the mixed-type anion framework is built of the AlO_5 and PO_4 polyhedra, while the columns of CuO_6 octahedra form the cationic part of the structure. The main fragment of the alluaudite $\text{KCuMn}_3(\text{VO}_4)_3$ structure is the cationic framework of MnO_6 octahedra and flat CuO_4 groups, which is reinforced with anionic VO_4 orthotetrahedra.

In the vanadyl-phosphate analogue of mahnertite $\text{K}_{2.5}\text{Cu}_5\text{Cl}(\text{PO}_4)_4(\text{OH})_{0.5}(\text{VO}_2) \cdot \text{H}_2\text{O}$, the copper and vanadi-

um operate as anion formers and build the anionic framework of mixed type together with PO_4 tetrahedra. The anion-forming function of amphoteric vanadium is also established in the structure of vanadate analogue of pyroxene $(\text{NH}_4)_2[(\text{V,P})_2\text{O}_6]$.

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References:

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