Poster Presentation

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Access to thermodynamically metastable polymorphs of Vanadium(III)Phosphate

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Reduction of β-VOPO4 [1] by moist hydrogen leads to two new metastable polymorphs of VPO4 ("m1" and "m2"). Two structure models for VPO4-m1 are proposed. The first one is based on the crystal structure of β-VOPO4. The second one is related to the crystal structures of the Lipscombite/Lazulite structure family, namely β-V2OPO4 and V4O3(PO4)3. Both structure models consist of PO4 tetrahedra sharing corners with square planar VO4 units. To the best of our knowledge this is the first example for V3+ in square-planar coordination by oxygen. Geometry optimization without symmetry constraints (PBE functional [2]) VPO4-m1 led to another new metastable polymorph of VPO4. The predicted structure consists of VO4 tetrahedra corner sharing with PO4 tetrahedra forming a 3D network.
The second metastable phase VPO4-m2 is isotypic to FeIIFeIII(VIVO)(P2O7)(PO4) [3]. DFT calculation (PBE functional [2]) allowed relaxation of the structure of VPO4-m2. Considering the interatomic distances obtained from DFT calculation the oxidatation states are V3+/V3+/V3+ instead of V2+/V3+/V4+. The average oxidation state of vanadium in VPO4-m2 is also V3+ which is suggested by the sealed tube experiments.

References
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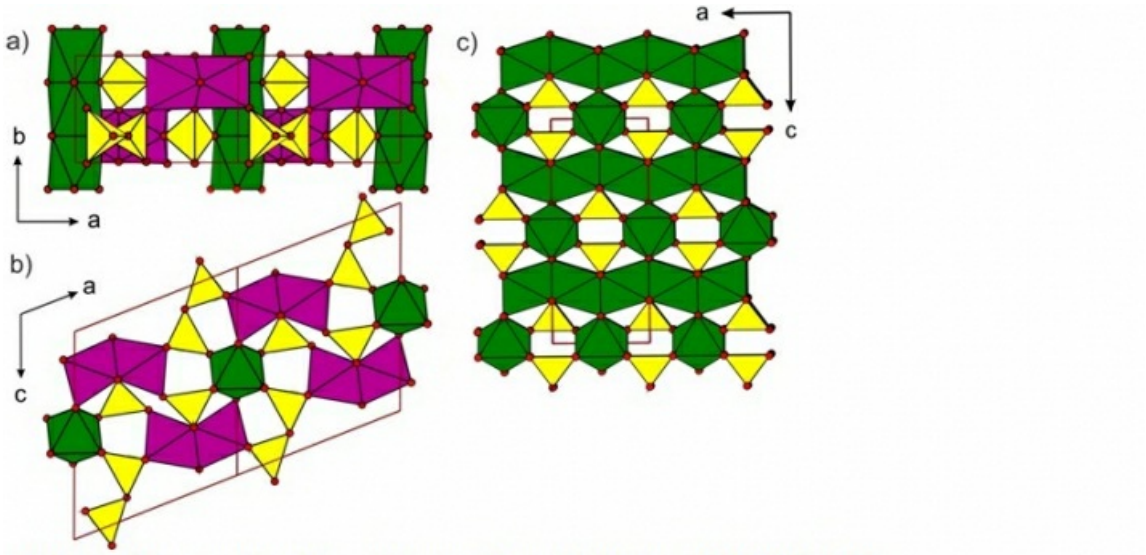

Fig.1 Polyhedral representation of the crystal structure of metastable VPO_4-m2, $V_2(VO)(P_2O_7)(PO_4)$ (a) and (b), and β-V_2OPO_4 (c). Green strings of phase sharing VO_6 octahedra, purple dimer of phase sharing VO_6 octahedra, and yellow PO_4 tetrahedra.

Keywords: metastable solids, crystal structure, solid state modelling