Reduction of $\beta$-VOPO$_4$ [1] by moist hydrogen leads to two new metastable polymorphs of VPO$_4$ ("m1" and "m2"). Two structure models for VPO$_4$-m1 are proposed. The first one is based on the crystal structure of $\beta$-VOPO$_4$. The second one is related to the crystal structures of the Lipscombite/Lazulite structure family, namely $\beta$-V$_2$OPO$_4$ and V$_4$O$_3$(PO$_4$)$_3$. Both structure models consist of PO$_4$ tetrahedra sharing corners with square planar VO$_4$ units. To the best of our knowledge this is the first example for V$^{3+}$ in square-planar coordination by oxygen. Geometry optimization without symmetry constraints (PBE functional [2]) VPO$_4$-m1 led to another new metastable polymorph of VPO$_4$. The predicted structure consists of VO$_4$ tetrahedra corner sharing with PO$_4$ tetrahedra forming a 3D network.

The second metastable phase VPO$_4$-m2 is isotypic to FeIIFeIII(VIVO)(P$_2$O$_7$)(PO$_4$)$_3$ [3]. DFT calculation (PBE functional [2]) allowed relaxation of the structure of VPO$_4$-m2. Considering the interatomic distances obtained from DFT calculation the oxidation states are V$^{3+}$/V$^{3+}$/V$^{3+}$ instead of V$^{2+}$/V$^{3+}$/V$^{4+}$. The average oxidation state of vanadium in VPO$_4$-m2 is also V$^{3+}$ which is suggested by the sealed tube experiments.

References

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