K$_2$Fe$_{\text{III}0.5}$Ti$_{\text{III0.5}}$Ti$_{\text{IV1.0}}$(PO$_4$)$_3$: Preparation and Characterization of a Langbeinite-related Phosphate Containing Iron(III) and Mixed-valent Titanium

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A potassium mixed iron(III)-titanium(III)-titanium(IV) phosphate K$_2$Fe$_{\text{III}0.5}$Ti$_{\text{III0.5}}$Ti$_{\text{IV1.0}}$(PO$_4$)$_3$ has been obtained using a two-step flux interaction in evacuated sealed silica tubes. It forms tetrahedrally-shaped dark violet crystals which belong to the cubic system (space group $P2_13$) with the cell parameter $a = 9.8592(5)$ Å. The structure was refined from single-crystal X-ray diffraction data. [MO$_6$] octahedra and [PO$_4$] tetrahedra share their vertices forming a rigid 3D framework. The potassium cations are located in large closed cavities of the framework. A distribution of the 3$d$ metals’ valence states in K$_2$Fe$_{\text{III}0.5}$Ti$_{\text{III0.5}}$Ti$_{\text{IV1.0}}$(PO$_4$)$_3$ has been proposed on the basis of magnetic measurements, structure investigations and bond-valence calculations as well as UV/vis and EPR spectroscopy.

Key words: Phosphate, Langbeinite, Flux Method, Mixed-valent, Magnetic Measurements