Crystal Structure, Polymorphism and Properties of the New Vanadylphosphate Na$_4$VO(PO$_4$)$_2$

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Reduced V-based mixed oxides with low-dimensional structures often exhibit interesting physical properties. This makes them very attractive objects for investigators. The new vanadylphosphate Na$_4$VO(PO$_4$)$_2$ was synthesized and investigated by X-ray powder and single crystal diffraction, high-temperature X-ray diffraction, electron diffraction, high resolution electron microscopy, thermal analysis, magnetic susceptibility and conductivity measurements. The compound undergoes a reversible phase transition at about 200 °C. The crystal structure of low-temperature β–Na$_4$VO(PO$_4$)$_2$ was solved using X-ray single crystal data. This phase has an orthorhombic unit cell with lattice parameters $a = 16.0068(12)$ Å, $b = 14.5129(8)$ Å, $c = 7.0231(5)$ Å, S.G. Pbca, $Z = 8$. The crystal structure of β–Na$_4$VO(PO$_4$)$_2$ is built by isolated chains formed by corner-shared V$^{4+}$O$_6$ octahedra linked additionally via corners by two PO$_4$ tetrahedra. All chains in the structure are equivalent. Na cations are located between the chains in an ordered manner. High temperature α–Na$_4$VO(PO$_4$)$_2$ also has an orthorhombic cell with lattice parameters $a = 15.595(1)$ Å, $b = 14.651(2)$ Å, $c = 7.0262(6)$ Å, S.G. Ibam, $Z = 8$. Electron diffraction study revealed an existence of various structural transformations occurring in situ in the transmission electron microscope. In both α– and β– modifications, the susceptibility follows a Curie-Weiss law with a very small Curie-Weiss temperature indicating a very weak magnetic exchange between the V$^{4+}$ ions.

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