Phase stability of V_6O_{13} and synthesis of defect mixed-valence $V_{0.92}O_2$ rutile at high pressures and temperatures

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Binary vanadium oxides exhibit a wide range of magnetic, electronic, and catalytic properties. Their magnetic and electronic transitions have recently been proposed for volatile resistive switching devices and neuromorphic computing [1]. The versatility of a vanadium cation to assume different valence states, its changing local environment, and the flexibility of the framework geometry of coordination polyhedra allow for the reversible intercalation of various ions, enabling, for instance, medical [2] or electrochemical [3] applications.

In this communication, we present our results on the high-pressure behaviour of the mixed-valence vanadium oxide V_6O_{13} that occurs in the *Wadsley* homologous series V_nO_{2n+1} between -V_2O_5 (*Pmmn*, $Z = 2$) and VO_2(B) ($C2/m$, $Z = 8$). The oxides in this series undergo metal-insulator phase transitions accompanied by orbital ordering. Their crystal structures could be derived from the *fcc* structure of VO_x, where $x \approx 1$ [4]. V_6O_{13} ($C2/m$, $Z = 2$) is composed of single and double layers formed by edge- and corner-sharing distorted VO_6 octahedra [5]. It could be described as being built of alternating VO_2(B)- and V_2O_5-like layers stacked along the *c* axis.

Upon compression at room temperature, V_6O_{13} is stable to at least 9.4 GPa as inferred from single-crystal synchrotron diffraction data [5]. *In-situ* synchrotron energy-dispersive powder diffraction provides the evidence that V_6O_{13} starts to amorphize and decomposes above 18.5 GPa at room temperature. It transforms to defect rutile-like phase $V_{0.92}O_2$ above 500 K in the pressure range up to about 15–17.5 GPa. The new material is recoverable to ambient conditions and its crystal structure ($C2/m$, $Z = 4$) is determined from laboratory single-crystal and powder X-ray diffraction data measured on single crystals grown at 10 GPa and 1373 K using a large-volume multi-anvil press. The vanadium atoms are at two non-equivalent split positions (Fig. 1). The V1 atoms are displaced from their ideal rutile-like position along the *b* axis. The V2 atoms are four-fold split in the (*b*,*c*) plane. The V2 sites are slightly more vanadium deficient than the V1 sites. The characteristic feature is the presence of two *zigzag* V–V chains. One of them has equidistant V atoms while the other is with short and long V–V distances.

The disordered structure of $V_{0.92}O_2$ is similar to those of the *M1*, *M2*, and *T* polymorphs of stoichiometric VO_2, in which the linear and/or *zigzag* chains arise from the distortions of the V sublattice [6]. The analysis of pseudo-symmetry indicate that the *M2* polymorph ($C2$/m, $Z = 8$), with alternate short and long distances in the linear V–V chain and with the V atoms equidistant in the other *zigzag* V–V chain, could be considered as the ordered (though distorted) variant of $V_{0.92}O_2$.

The results of our study show that it is possible to obtain non-stoichiometric rutile-related phases of VO_2 at extreme conditions. It remains to be seen how their physical properties and phase transformations are influenced by their chemical composition.

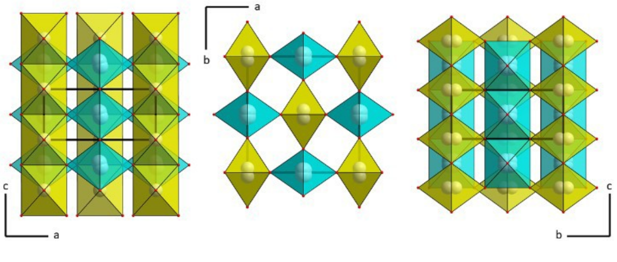

Fig. 1 - Crystal structure of $V_{0.92}O_2$. The octahedra around the V1 and V2 atoms are drawn in yellow and cyan, respectively.

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