High-pressure crystal structures of Wadsley-type vanadium oxides V_2O_5 and V_6O_{13}

B. Viliam Hakala (b.hakala@fz-juelich.de) [1, 2], Dimitra K. Manousou [3], Karen Friese [1], Konstantin Glazyrin [4], Wilson A. Crichton [5], Andrzej Grzechnik[2]

[1]Jülich Centre for Neutron Science-2 and Peter Grünberg Institute-4 (JCNS-2/PGI-4), Forschungszentrum Jülich GmbH, Germany; [2]Institute of Crystallography, RWTH Aachen, Aachen, Germany; [3]Section of Condensed Matter Physics, Department of Physics, National and Kapodistrian University of Athens, Athens, Greece; [4]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany; [5]The European Synchrotron Radiation Facility (ESRF), Grenoble, France

The so-called Wadsley phases with general formula V_nO_{2n+1} form a homologous series of compounds [1,2]. They have arisen much interest due to the observed metal-insulator transitions and their potential application as battery materials. The crystal structures of the parent compound V_2O_5 and of V_6O_{13} (*n=3*) at ambient conditions are closely related, being built up of edge and corner sharing building units, which can be described as $[VO_5]$-pyramids in V_2O_5 (space group *Pmmn*) and as $[VO_6]$-octahedra in V_6O_{13} (space group *C2/m*) [3,4].

High pressure Raman and powder diffraction investigations on V_2O_5 suggest a pressure-induced phase transition between 4 and 7 GPa [5,6]. A recent *in-situ* high-pressure powder diffraction study suggests an irreversible phase transition from α-V_2O_5 to an amorphous state around 12.6 GPa while according to other investigations V_2O_5 becomes only fully amorphous under 20.2 GPa [7]. Under high-temperature high-pressure conditions α-V_2O_5 converts into β-V_2O_5 (*$P2_1/m$)* [8]. Ex-situ high-pressure high-temperature synthesis in a multi anvil press yielded δ-V_2O_5 (*C2/c)* which is isostructural to Sb_2O_5[9]. Despite the high level of interest high pressure investigations using single crystal diffraction have not been performed, nor was the HP-HT phase diagram of V_2O_5 studied *in situ* up to know. In addition, despite the fact that the low temperature metal-insulator transition in V_6O_{13} has been very well studied [10,11], high pressure investigations have not been performed so far on this compound.

We have now studied single crystals of V_2O_5 and V_6O_{13} as a function of pressure at Petra III, Desy. The studies on V_2O_5 show complete irreversible amorphization of the sample above 7.3 GPa and, moreover, anomalies are observed between 3 and 4 GPa. To further investigate the HP-HT behaviour of V_2O_5, we used the large volume press at ID06 at the ESRF and followed the evolution of the sample with *in-situ* synchrotron radiation. Heating of the amorphous phase lead to the formation of the δ-V_2O_5 polymorph with Sb_2O_5 structure, which can be recovered at ambient conditions. High pressure single crystal diffraction experiments on V_6O_{13} show an anomalous behaviour between 2 and 3 GPa, yet the ambient pressure polymorph seems to be stable up to the highest pressures reached in the experiment.

[1] Schwingenschlögl, U. et al. Ann. der Phys. 13, 475–510 (2004)
[2] Eguchi, R. et al. Phys. Rev. B - Condens. Matter Mater. Phys. 65, 1–4 (2002)
[3] Enjalbert, R. et al. Acta Crystallogr. Sect. C Cryst. Struct. Commun. 42, 1467–1469 (1986)
[4] Wilhelmi, K.A. et. al., Acta Chemica Scandinavica 25, 2675-2687 (1971)
[5] Grzechnik, A. Chem. Mater. 10, 2505–2509 (1998)
[6] Loa, I. et al. J. Alloys Compd. 317–318, 103–108 (2001)
[7] Zou, Y. et al. J. Alloys Compd. 790, 164–169 (2019)
[8] Filonenko, V. P. et al. Acta Cryst. B60, 375–381 (2004)
[9] Zibrov, I. P. et al. High Press. Res. 33, 399–408 (2013)
[10] Kimizuka, N. et. al., Acta Cryst. B34, 1037-1039 (1978).
[12] Höwing, j. et. al., Acta Cryst. B59, 747-752 (2003).

B.V.H. and K.F. acknowledge support by the Deutsche Forschungsgemeinschaft (SFB 917).