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Oxygen Deficient Lead-Technetium Pyrochlore, the First Example of a Stable Valence V Technetium Oxide?

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Despite the fact that Technetium V oxides are possible there are very few reports of their existence. Most recently Lawler et.al. [1] have reported the structure of Tc_2O_5 "tech red" and have noted that it is indeed volatile. It is apparent from this study that there is no stable form and they draw parallels with a well-studied analogue of Tc_2O_5, Re_2O_5 that disprortioniates into Re(4+) and Re(7+) species. Given these parallels we investigated PbTcO3 as reported by Muller et.al [2] to be a pyrochlore in an attempt to determine if there were parallels with $Pb_2Re_2O_{7-d}$. The structure of lead-technetium pyrochlore has been refined in space group with a = 10.36584(2) Å using a combination of synchrotron X-ray and neutron powder diffraction data and confirmed via Electron Diffraction. The oxide is found to be oxygen deficient with a stoichiometry of $Pb_2Tc_2O_{6.86}$. The displacive disorder of the Pb cations is evident from the refinements as has been observed $Bi_2Tc_2O_{7-d}$. X-ray absorption measurements at the Tc K-edge demonstrate the valence of the Tc is greater than 4.0 as anticipated from the refined oxygen stoichiometry. Raman spectroscopy confirms the local coordination of the Technetium leading us to conclude that this pyrochlore is the first example of a stable valence V Technetium oxide.

[1] Lawler, K. V. *et al.* Unraveling the mystery of 'tech red'-a volatile technetium oxide. *Chem. Commun.* **54**, 1261–1264 (2018).

[2] Muller, O., White, W. B. & Roy, R. Crystal chemistry of some technetium-containing oxides. *J. Inorg. Nucl. Chem.* **26**, 2075–2086 (1964).