

Topochemical conversion of layered tungstates: an in-situ Raman spectroscopy and total scattering study

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Topochemical conversions of layered compounds via *chemie douce* routes hold great potential to effectively design new materials, especially in the vast chemical field of perovskites [1]. The possibility to target metastable structures which are inaccessible by conventional solid-state reactions is a particular advantage. Such an example exists in the layered tungstate family, which is well known for their photocatalytic properties. Aurivillius-type $\text{Bi}_2\text{W}_2\text{O}_9$ converts to Ruddlesden-Popper-type $\text{H}_2\text{W}_2\text{O}_7$ via hydrochloric acid treatment [2,3]. The structural peculiarities of the highly disordered product are not fully resolved, yet. $\text{H}_2\text{W}_2\text{O}_7$ decomposes to WO_3 above 400 K, preventing post-synthesis calcination to increase crystallinity. Only very recently a consistent structural model was proposed [4]. Deeper understanding of the leaching process could help in optimizing the synthesis conditions to yield products of higher crystallinity. Previous results suggest a selective leaching of the $\text{Bi}_2\text{O}_2^{2+}$ -layer present in the parent compound while retaining the inert perovskitic $\text{W}_2\text{O}_7^{2-}$ -layer. Kudo et al. [3] based the selective leaching mechanism on the low amount of dissolved tungsten in the reaction liquid and comparable particle morphology of educt and product. However, changes in the atomic structure over the course of the reaction have not been investigated for these tungstates so far.

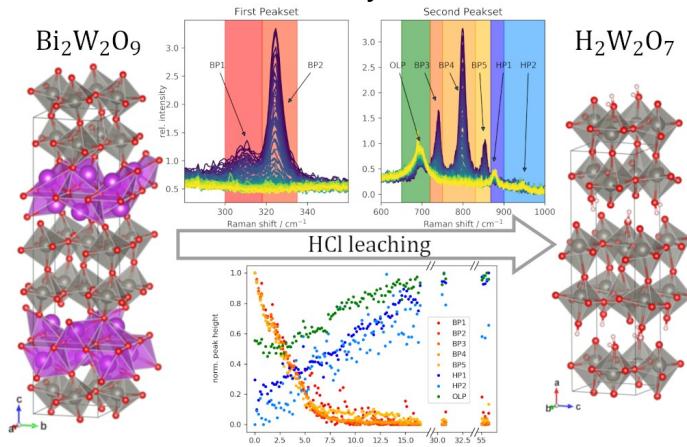


Fig. 1: Evolution of Raman spectra during conversion

Here we present an *in-situ* Raman spectroscopic study of the leaching process which is further supported by *ex-situ* total scattering experiments and pair-distribution function analysis. Signals attributed to $\text{Bi}_2\text{O}_2^{2+}$ -layers vanish fast while features of the $\text{W}_2\text{O}_7^{2-}$ -layer are constantly present, supporting the proposed mechanism. Furthermore, the evolution of the product signals is delayed with respect to the vanishing of educt features. This indicates a structural decoherence as the $\text{Bi}_2\text{O}_2^{2+}$ -layer is broken down significantly faster than the $\text{H}_2\text{W}_2\text{O}_7$ stacks reform, resulting in a loss of long-range order. Our results confirm and extend previous reports and also point further research towards investigating an alignment of break-down and build-up reaction rates.

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