Bridging manganese clusters and materials formation: Polymorphism control in manganese oxide nanoparticles in hydrothermal synthesis

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Manganese oxides can adopt several stoichiometries thanks to the relative stability of the Mn ion in oxidation states +2, +3 and +4, and accommodate cations of different sizes, leading to a range of different layered and tunneled crystal structures. [1, 2] Each of these phases have distinct properties, and synthetic control of polymorph formation is crucial. Here, we use *in situ* X-ray total scattering and PDF analysis supported by *in situ* XANES to study the formation mechanism leading to different manganese oxide polymorphs during hydrothermal synthesis. PDF analysis allows to follow structural changes all the way from the precursors in solution to the final product. We show that by changing the ratio between manganese(II) salt and oxidizer, it is possible to not only select between R and α-MnO_2, but more importantly the formation mechanism differs as well. Furthermore, we show that these processes involve intermediate manganese oxido-clusters, structurally similar to those found in nature or in molecular magnets,[3, 4] which act as building blocks in the formation of the crystalline nanoparticles.

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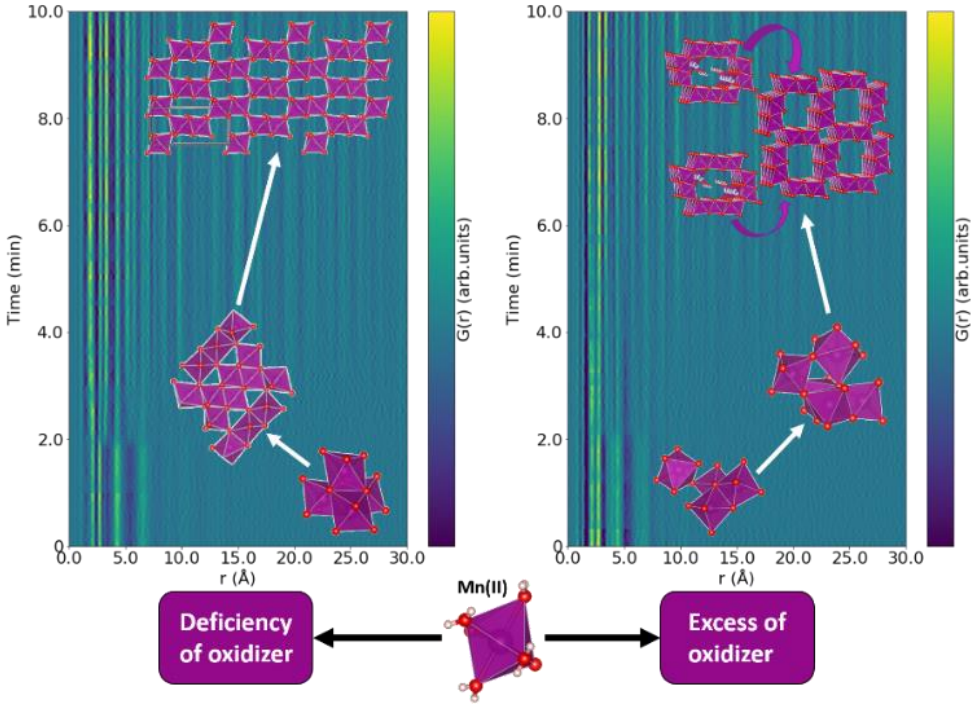
3. Yano, J. and V.K. Yachandra, *Mn4Ca cluster in photosynthesis: where and how water is oxidized to dioxygen.* Chemical Reviews, 2014. **114**(8): p. 4175-4205.
4. Charalambous, M., et al., *[Mn14] "Structural Analogues" of Well-Known [Mn12] Single-Molecule Magnets.* European Journal of Inorganic Chemistry, 2018. **2018**(35): p. 3905-3912.

Manganese oxide; crystallization pathway; metal-oxido cluster; in situ Pair Distribution Function; hydrothermal synthesis



By changing the ratio between manganese(II) salt and oxidizer, different reaction pathways occur, leading to either R- or α-MnO_2