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# Electronic Supplementary Information

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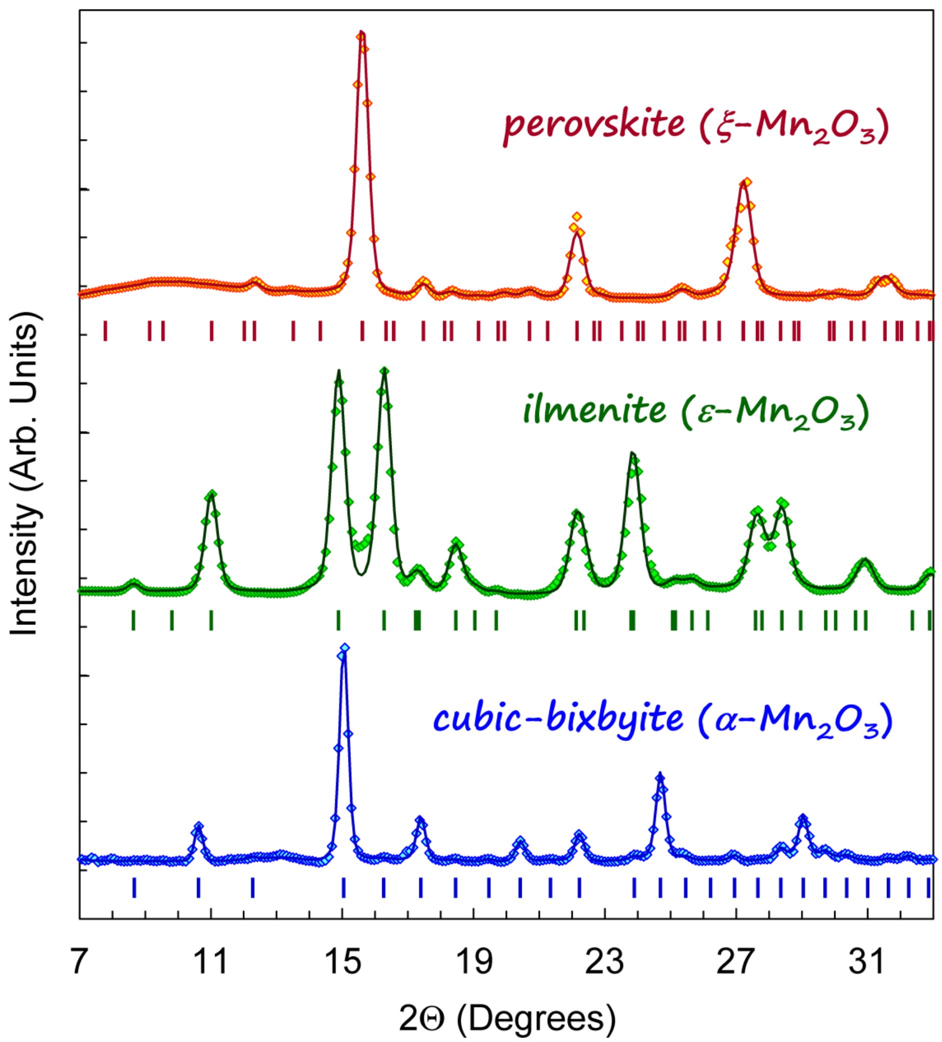
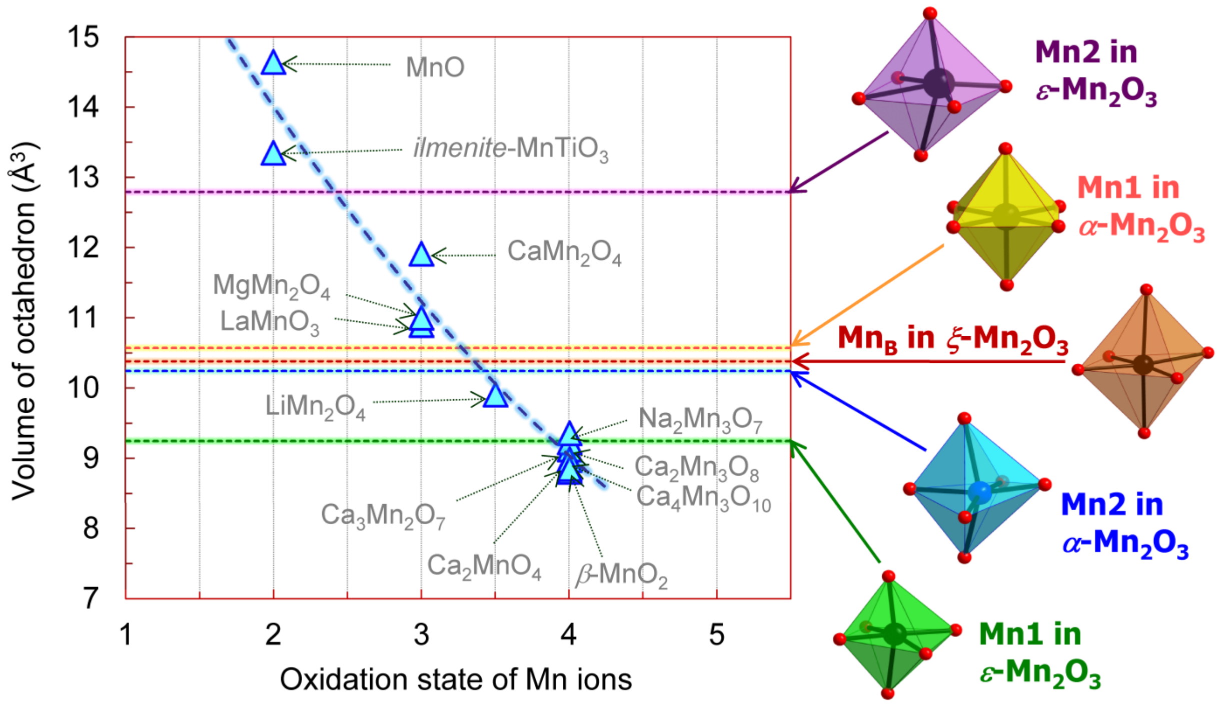



**Supplementary Figure 1.** Comparative powdery x-ray diffraction patterns of the starting powder of the cubic-bixbyite phase ($\alpha$-$Mn_2O_3$), and of the samples synthesized under high-pressure high-temperature conditions adopting the ilmenite-type ($\varepsilon$-$Mn_2O_3$) and the perovskite-type ($\xi$-$Mn_2O_3$) structures, acquired at ambient conditions. The symbols are experimental data, the solid lines are calculated profiles, and the dashes are anticipated reflections. For simplicity, the perovskite phase has been indexed not in triclinic, but in an alternative rhombohedral $R\overline{3}$ symmetry, also suggested for this phase.[1] Note that these structural examinations were conducted only to identify the phases in the synthesized samples, since their crystals structures have been already investigated in detail in previous studies.[1,2]




**Supplementary Figure 2.** Correlation between the volume of oxygen octahedron of a Mn ion and its oxidation state at normal conditions. Blue triangles are data for Mn-bearing oxides for which the oxidation state of the Mn ion is precisely known. We analysed available structural data from the FIZ Karlsruhe database (https://www.ccdc.cam.ac.uk/structures/) for manganese oxides comprising cations with well-known oxidation states, namely, $Na^+$, $Li^+$, $Ca^{2+}$, $Mg^{2+}$, $La^{3+}$, and $Ti^{4+}$. These data suggest a correlation between the octahedron volume and oxidation state. A polynomial fit of these data is shown by a dashed blue line. Horizontal dashed lines show the volumes of oxygen octahedrons in the binary $Mn_2O_3$ oxides we studied (cubic-bixbyite $\alpha$-$Mn_2O_3$, ilmenite $\varepsilon$-$Mn_2O_3$, perovskite $\xi$-$Mn_2O_3$). These lines are labelled on the right side of the plot.


References:

1) S. V. Ovsyannikov, A. M. Abakumov, A. A. Tsirlin, W. Schnelle,R. Egoavil, J. Verbeeck, G. Van Tendeloo, K. V. Glazyrin, M. Hanfland and L. Dubrovinsky, *Angewandte Chemie International Edition*, 2013, **52**, 1494–1498.

2) S. V. Ovsyannikov, A. A. Tsirlin, I. V. Korobeynikov, N. V. Morozova, A. A. Aslandukova, G. Steinle-Neumann, S. Chariton, S. Khandarkhaeva, K. Glazyrin, F. Wilhelm, A. Rogalev and L. Dubrovinsky, *Inorganic Chemistry*, 2021, **60**, 13348–13358.