

# Supporting Information

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## Synthesis

The two suites of samples were produced by the laboratory of one of the authors (M.M.N.) using similar starting solutions with different Ca and Mn concentrations. For both suites of samples, the first sample was made at 0 °C and each subsequent sample was produced at a temperature ~20 °C higher (IR temperature probe) than the temperature of the previous sample. Additionally, each subsequent sample synthesis involved an increase in the amount of potassium hydroxide (KOH) by 10 g, starting with 10 g of KOH for the first sample reaction in ~400 mL of 18-M $\Omega$  water. For both sample suites, a starting concentration of calcium to manganese in the reaction reagents reflected that of the final sample composition (Table 1). The resulting products were extremely fine particulates. The reactions were complete within about 2 h, but the products were allowed to wet-age for an additional 6 h. The particulates were recovered from the aqueous reaction matrix using centrifugation (660  $\times$  g for 12 min) and subsequently washed by means of the addition of 18-M $\Omega$  water until the rinses were no more than 0.14 mS (conductivity meter), which indicated all extraneous ions were washed away from the product. The samples were dried in a vacuum drier at room temperature to complete dryness (~18 h for 500-mg amount of sample). Chemical analysis by actively coupled plasma (ICP) optical emission spectrometry (OES) indicated no presence of potassium in any of the samples. The samples were not specially treated intentionally to modify the average oxidation state (AOS) of manganese; that was all Mother Nature's doing.

## Characterization

**High-Temperature Oxide-Melt Solution Calorimetry.** Solution calorimetric studies of nanoparticles of varying size provide a direct measurement of the variation of enthalpy with surface area; a linear relation implies a constant surface enthalpy (SE; surface energy) (1–5). Because oxides are generally poorly soluble in aqueous solvents, the well-established technique of high-temperature oxide-melt solution calorimetry, in which small pellets of sample are dropped from room temperature into a molten oxide solvent held in the calorimeter at high temperature, was used to dissolve the oxides and to control the final oxidation state (6, 7). The measured enthalpy, called the heat of drop solution,  $\Delta H_{ds}$ , contains several contributions: the heat content of the sample, its enthalpy of dissolution at calorimetric temperature, and any enthalpy of oxidation-reduction or gas evolution associated with the process. To interpret the data properly, both the initial state (chemical composition, structural state, and surface area of the solid sample) and the final state (complete dissolution, changes in oxidation state, and evolution of gases) must be characterized. Additionally, surface water contributes to the total heat effect and must be accounted for, as previously described (8). Contribution of bulk H<sub>2</sub>O was subtracted from the experimental enthalpy using the appropriate thermochemical cycle as discussed below. The slope of the line relating the water-corrected heat of solution to surface area provided the SE. When the enthalpy associated with the H<sub>2</sub>O is taken as that of bulk water for the process H<sub>2</sub>O (liquid, 25 °C)  $\rightarrow$  H<sub>2</sub>O (gas, 700 °C), the calculated SE represents the enthalpy of the hydrated surface (1, 9). We note that the SE is essentially the same as the surface energy and is a good representation of the surface free energy because both the volume change and entropy change on forming nanoparticles from bulk material are small (10, 11).

**Manganese AOS and Manganese Speciation.** Titration of Mn(III) and Mn(IV) oxidation states used a modified Murray method (12). We describe here the methods of standardization and ti-

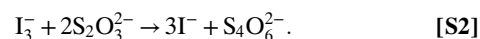
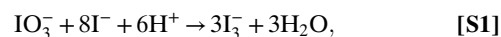
tration in addition to detailing calculations for both manganese AOS and manganese speciation. As far as we know, this information is not detailed elsewhere in the literature and is not taught as a standard analytical chemistry procedure. We provide the details so that a potential user does not have to do an extensive literature survey.

The method involves iodometry, which has become widely used after its development from the Winkler method (13) for dissolved oxygen measurement in aqueous media. Iodometric titrations for manganese AOS determination were first presented by Murray (12); hence, we refer to the method of manganese oxidation state titration as Murray titration. The procedure involves the reaction of dissolved manganese ions with a large excess of iodide (I<sup>-</sup>) in an acidic medium to produce triiodate (I<sub>3</sub><sup>-</sup>), which is then titrated with a standardized solution of S<sub>2</sub>O<sub>3</sub><sup>(2-)</sup>. This method was used successfully to measure manganese AOS in natural manganese oxides (Mn-oxides) and ferromanganese oxides of medium-range order mineral structure phases (12), as well as in bacteriogenic layered Mn-oxides (14); thus, the method should translate well to synthetic layered structure Mn-oxides.

The method titrates the iodine produced by reaction of iodide with manganese ions directly and can be performed at room temperature. The titrant solution is highly concentrated in I<sup>-</sup>. I<sub>3</sub><sup>-</sup> is formed according to the equilibrium I<sub>2</sub> + I<sup>-</sup>  $\rightarrow$  I<sub>3</sub><sup>-</sup>, where I<sub>2</sub> is molecular iodine. Because I<sub>2</sub> is volatile, an excess of iodide (as sodium iodide) must be present in the acidified aqueous matrix containing the manganese ions from the sample to maintain the iodine as a water-stable I<sub>3</sub><sup>-</sup> complex. After the redox reaction is complete between the Mn ions with an excess of I<sup>-</sup> to produce I<sub>3</sub><sup>-</sup>, the resulting iodine is titrated with a volume of standardized thiosulfate solution. The number of moles of thiosulfate that react with the I<sub>3</sub><sup>-</sup> provides the number of moles of manganese that are reduced during the process of iodide oxidation by manganese species having a greater than +2 oxidation state (aqueous manganese cannot be further reduced than to divalent).

It is important to note that the use of nitrogen gas-sparged 18-M $\Omega$ /cm water drives off dissolved gases from the aqueous matrix that may oxidize some portion of the excess iodide. Another potential source of error for the titration is the volatility of iodine, which can effectively be prevented by adding excess iodide and by keeping all solutions at a temperature not exceeding 25 °C. Nitrite and copper ions, in addition to UV light, will catalyze conversion of iodide to iodine; thus, exposure to these must be minimized. For protracted titrations, some analytical chemists suggest addition of dry ice to the titration mixture to displace air from the Erlenmeyer flask to prevent air oxidation of iodide to iodine. Calculations of manganese AOS and manganese speciation in the calcium manganese oxide (CaMnO) samples require that the total composition of manganese, as well as calcium, be known for each sample. Total Mn and total Ca can be measured using different analytical methods (ICP-MS, ICP-OES, or microprobe).

Two chemical equilibrium equations are involved in the standardization process:



Iodate (IO<sub>3</sub><sup>-</sup>) is the primary standard used to standardize a sodium thiosulfate secondary standard solution. An I<sub>3</sub><sup>-</sup> ion is obtained from the primary standard [potassium iodate (KIO<sub>3</sub>)], and 3 mol of I<sub>3</sub><sup>-</sup> is obtained in solution for each IO<sub>3</sub><sup>-</sup> ion (3:1

ratio). However, the iodine species that is reactive in an aqueous matrix exists not as iodate  $\text{IO}_3^-$  ion, molecular iodine  $\text{I}_2$ , or iodide  $\text{I}^-$ ; instead, it exists as  $\text{I}_3^-$ , which is what reacts with the thiosulfate  $[\text{S}_2\text{O}_3^{2-}]$ . Thus, 2 mol of  $\text{S}_2\text{O}_3^{2-}$  is required to neutralize each mole of  $\text{I}_3^-$ . Further details of the titration procedure are given below.

Step 1 is to prepare unstandardized sodium thiosulfate solution (also known as a secondary standard). For a 0.05- to 0.06-M solution of sodium thiosulfate, dissolve ~12 g of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (158.11 g/mol) in 1 L of freshly nitrogen gas-sparged 18-M $\Omega$  water. Sparging the 18-M $\Omega$  water with nitrogen gas drives off other dissolved gas species, which may be redox-active or may alter the pH. If the thiosulfate solution is too concentrated to obtain at least a 20-mL end point titration volume for the analysis, one must do a simple dilution and then double-check the standardization against a reference material ( $\text{MnO}_2$  of 99.99% purity from Sigma–Aldrich). The thiosulfate stock solution must be re-irradiated to maintain freshness for up to a few weeks.

Step 2 is to prepare the treated iodate primary standard solution:

- The primary standard  $\text{KIO}_3$ , available as a standard solution (Sigma–Aldrich), is chemically treated to obtain the stabilized  $\text{I}_3^-$  species in water. A slight excess of  $\text{I}^-$  is supplied by dissolving solid potassium iodide (KI). The  $\text{H}^+$  can be supplied by adding a nonreactive acid, such as  $\text{H}_2\text{SO}_4$ . Starch indicator solution is prepared by dissolving 2 g of laboratory-grade soluble starch in 100 mL of hot distilled water, which is then stored in a medicine dropper bottle and kept under refrigeration.
- Twenty-five milliliters of 0.1-N (0.01 M)  $\text{KIO}_3$  ( $M_r = 214$ ) Primary Standard solution (Sigma–Aldrich) is pipetted into a 250-mL Erlenmeyer flask.
- Two grams of KI ( $M_r = 166$ ) is added and stirred well using a magnetic stir bar to dissolve all solids.
- Approximately 5 mL of 2 M  $\text{H}_2\text{SO}_4$  is added to the solution, which is now ready to standardize the thiosulfate solution.

Step 3 is standardization of sodium thiosulfate secondary standard solution. The standardization of  $\text{Na}_2\text{S}_2\text{O}_3$  occurs according to Eq. S2. The unstandardized thiosulfate solution is placed into a prepared 50.00-mL buret. Starch indicator is used to accentuate the end point and is added near the end of the titration, when the titrated solution is pale yellow (often referred to as straw-colored). Addition of the starch indicator, which complexes with solution iodine, produces black-blue solution coloration. When the end point is reached, in which all iodine has been reduced, the solution turns clear. Use the titrated volume to compute the actual molarity of the thiosulfate solution, and it is now standardized.

The steps of the Murray titration are described below for measuring the Mn-oxide samples.

To a 100-mL Erlenmeyer flask add:

- Fifty milliliters of degassed, chilled 18-M $\Omega$ /cm water
- A weighed sample of ~50 mg of the Mn-oxide sample

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$$\alpha = 2 - [(\text{Volume of } \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Concentration of } \text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Molar mass of Mn-oxide sample}) / (\text{mass of Mn-oxide sample})].$$


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- Ten milliliters of sodium iodide (NaI) (or KI) excess reagent solution (70 g of NaI in 100 mL of degassed 18-M $\Omega$ /cm water)
- Five milliliters of 2 M  $\text{H}_2\text{SO}_4$

The Mn-oxide sample dissolves in about 15 min (stirring will aid this process). Note that the standard reference  $\text{MnO}_2$  requires

more time to dissolve due to coarseness. The resulting solution is titrated with a triply standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

For computing errors in manganese AOS, we report two SEs of measurement for each sample based on triplicate experiments. Although these errors are in the range of  $\pm 0.001$  to  $\pm 0.005$ , we report the error as  $\pm 0.01$  due to the limitations in measurement imposed by likely uncertainties in the volumetric glassware.

**Calculations to Obtain Manganese AOS.** Total oxidized equivalents, [OX], of manganese may be expressed as the manganese AOS obtained from the Murray titration:

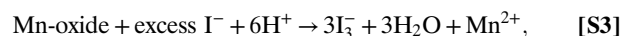
$$[\text{OX}] = 2 * [\text{Mn(IV)}] + [\text{Mn(III)}].$$

Subsequently, the O/Mn ratio, as in  $\text{MnO}_x$ , is calculated as:

$$x = 1 + 1/2 * [(\text{Total oxidized equivalents}) / (\text{Total moles of Mn})],$$

where “total moles of Mn” is obtained from ICP-MS and “Total oxidized equivalents” is obtained from the Murray titration. In terms of  $x$ , 2 SDs of the mean can be very low (less than 0.002) with strict adherence to proper analytical methodology. Although a buret may only be read to an accuracy of 0.01 mL, the reproducibility of the method is outstanding.

In summary, this method determines the total oxidized equivalents from the moles of thiosulfate standard that went into the reaction. One then uses this value to compute both the O/Mn ratio and the manganese oxidation state speciation. In the present context then, the use of Eqs. S1 and S2 may be modified slightly to reflect the Mn-oxide as the oxidizing agent, and the resulting iodine species is titrated with thiosulfate to determine the moles of equivalent electrons that were involved in this process:



The Mn-oxide reacts with the iodide to produce iodine. This liberated iodine then gets titrated with a standardized sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) solution to a colorimetric end point (in this case, until complete disappearance of color). From the volume and concentration of titrated thiosulfate, the sample mass, and sample formula weight, we obtain the value for total oxidized equivalents.

**Calculations for Manganese Speciation.** For manganese speciation (the number of manganese atoms in each oxidation state in the sample or analyte solution), we need to compute fractions of each Mn oxidation state relative to the total manganese content. This speciation is directly related to the total number of moles of electrons transferred during iodometric titration. We call the mole fraction of  $\text{Mn}^{3+}$   $\alpha$  and that of  $\text{Mn}^{4+}$   $\beta$ , where  $\beta = (1 - \alpha)$ . From the Murray titration,

Then,

$$[\text{Manganese AOS}] = 2 * [\text{Mn(IV)}] + [\text{Mn(III)}] = 2 * [(4 * \beta) + (3 * \alpha)].$$

The ratio of oxygen to manganese remains O/Mn =  $1/2 * (\text{Mn AOS})$ . Furthermore, Ca is always in the +2 oxidation state,

which contributes one oxygen per calcium to the chemical formula. The chemical formula of the compound, normalized to 1 mol of Mn, neglecting water, is given by:

$$m\text{Ca} \cdot \alpha\text{Mn(III)} \cdot \beta\text{Mn(IV)} \cdot \text{O} \cdot [(2 \cdot m\text{Ca}) + 3 \cdot \alpha + 4 \cdot \beta]/2,$$

where  $m = [(\text{total wt\% Ca in sample}/\text{Ca atomic mass})/(\text{total wt\% Mn in sample}/\text{Mn atomic mass})]$ .

$$\begin{aligned} &(\text{Ca}_m\text{MnO}_{(1.5+m+0.5y)} \cdot n\text{H}_2\text{O})_{(\text{nano},25^\circ\text{C})} \rightarrow \text{Ca}_m\text{MnO}_{(1.5+m+0.5y)}(\text{sln},700^\circ\text{C}) + n\text{H}_2\text{O}_{(\text{gas},700^\circ\text{C})} = \Delta H_1 = \Delta H_{\text{ds}} \\ &n\text{H}_2\text{O}_{(\text{gas},25^\circ\text{C})} \rightarrow n\text{H}_2\text{O}_{(\text{gas},700^\circ\text{C})} = \Delta H_2 = n(25.0 \pm 0.1 \text{ kJ/mol})^{(15)} \\ &n\text{H}_2\text{O}_{(\text{liq},25^\circ\text{C})} \rightarrow n\text{H}_2\text{O}_{(\text{gas},25^\circ\text{C})} = \Delta H_3 = n(44.0 \pm 0.1 \text{ kJ/mol})^{(15)} \\ &(\text{Ca}_m\text{MnO}_{(1.5+m+0.5y)} \cdot n\text{H}_2\text{O})_{(\text{nano},25^\circ\text{C})} \rightarrow (\text{Ca}_m\text{MnO}_{(1.5+m+0.5y)} \cdot n\text{H}_2\text{O})_{(\text{sln},700^\circ\text{C})} = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3. \end{aligned}$$

Here, sln means dissolved in  $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$  at  $700^\circ\text{C}$ .  $\Delta H_1 = \Delta H_{\text{ds}}$  denotes values obtained using high temperature oxide melt solution calorimetry.  $\Delta H_2$  is the heat content of water as it is changing temperature over the range  $25^\circ\text{C}$  to  $700^\circ\text{C}$  (15).  $\Delta H_3$

**Thermochemical Cycles and Calculations. Surface enthalpy.** First, we give the thermochemical cycle for bulk water correction for the  $\text{CaMnO}$  phases:  $\text{Ca}_m\text{MnO}_{(1.5+m+0.5y)} \cdot n\text{H}_2\text{O}$ . Here, Mn(IV) is represented by “y” and Mn(III) is represented by  $(1 - y)$  because all calculations refer to 1 mol of manganese. The coefficients “m” and “n” account for moles of calcium and moles of water contained in the samples, respectively:

is the enthalpy of condensation (15). This water-corrected enthalpy of drop solution ( $\Delta H_4$ ) is plotted against molar surface area, and the slope of the line gives the SE of the hydrated surface.

#### Enthalpy of formation from oxides $\text{CaO}$ , $\text{Mn}_2\text{O}_3$ , $\text{MnO}_2$ , and $\text{H}_2\text{O}$ .

$$\begin{aligned} &m\text{CaO}_{(\text{s},25^\circ\text{C})} \rightarrow m\text{CaO}_{(\text{sln},700^\circ\text{C})} = \Delta H_1 = m \cdot (-90.7 \pm 1.69 \text{ kJ/mol})^{(16)} \\ &1/2(1-y)\text{Mn}_2\text{O}_3(\text{s},25^\circ\text{C}) \rightarrow 1/2(1-y)\text{Mn}_2\text{O}_3(\text{sln},700^\circ\text{C}) = 1/2(1-y) \cdot \Delta H_2 = 1/2(1-y) \cdot (154.87 \pm 1.00 \text{ kJ/mol})^{(17)} \\ &y\text{MnO}_2(\text{s},25^\circ\text{C}) \rightarrow y\text{MnO}_2(\text{sln},700^\circ\text{C}) = y \cdot \Delta H_3 = y \cdot (124.92 \pm 1.03 \text{ kJ/mol})^{(17)} \\ &n\text{H}_2\text{O}_{(1,25^\circ\text{C})} \rightarrow n\text{H}_2\text{O}_{(\text{g},700^\circ\text{C})} = n \cdot \Delta H_4 = n \cdot (69.0 \pm 0.1 \text{ kJ/mol})^{(15)} \\ &m\text{CaO} \cdot 1/2(1-y)\text{Mn}_2\text{O}_3 \cdot y\text{MnO}_2 \cdot n\text{H}_2\text{O}_{(\text{s},25^\circ\text{C})} \rightarrow \left[ m\text{CaO} + 1/2(1-y)\text{Mn}_2\text{O}_3 + y\text{MnO}_2 \right]_{(\text{sln},700^\circ\text{C})} + n\text{H}_2\text{O}_{(\text{g},700^\circ\text{C})} = \\ &\Delta H_5 = \Delta H_{\text{ds}} \text{ sample kJ/mol.} \\ &\left[ m\text{CaO} + 1/2(1-y)\text{Mn}_2\text{O}_3 + y\text{MnO}_2 \right]_{(\text{s},25^\circ\text{C})} + n\text{H}_2\text{O}_{(1,25^\circ\text{C})} \rightarrow m\text{CaO} \cdot 1/2(1-y)\text{Mn}_2\text{O}_3 \cdot y\text{MnO}_2 \cdot n\text{H}_2\text{O}_{(\text{s},25^\circ\text{C})} = \\ &\Delta H_{\text{f-ox}}^* \text{ kJ/mol} \end{aligned}$$

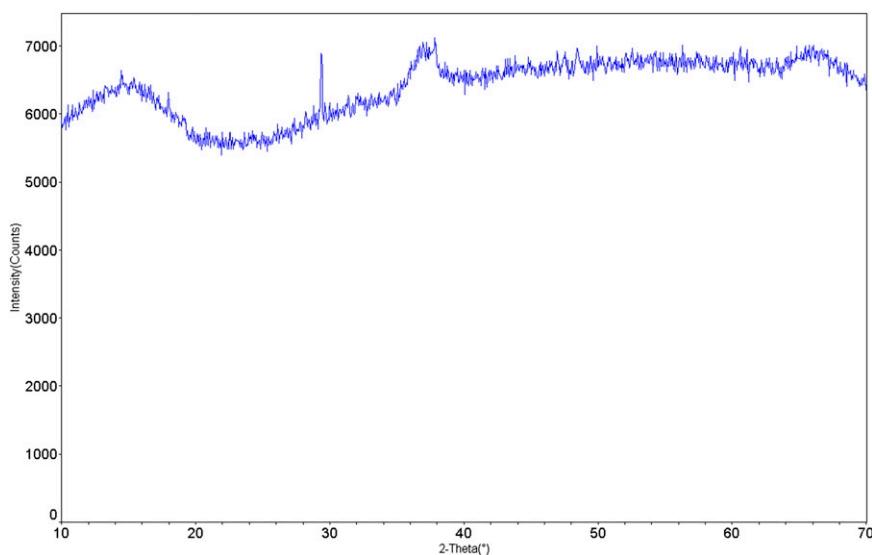
#### Enthalpy of formation from oxides $\text{CaO}$ , $\text{Mn}_2\text{O}_3$ , $\text{H}_2\text{O}$ , and $\text{O}_2$ .

$$\begin{aligned} &m\text{CaO}_{(\text{s},25^\circ\text{C})} \rightarrow m\text{CaO}_{(\text{sln},700^\circ\text{C})} = m \cdot \Delta H_1 = m \cdot (-90.7 \pm 1.69) \text{ kJ/mol}^{(16)} \\ &1/2\text{Mn}_2\text{O}_3(\text{s},25^\circ\text{C}) \rightarrow 1/2\text{Mn}_2\text{O}_3(\text{sln},700^\circ\text{C}) = 1/2 \cdot \Delta H_2 = 1/2 \cdot (154.87 \pm 1.00) \text{ kJ/mol}^{(17)} \\ &1/4y\text{O}_2(\text{s},25^\circ\text{C}) \rightarrow 1/4y\text{O}_2(\text{g},700^\circ\text{C}) = 1/4y \cdot \Delta H_3 = 1/4y \cdot (21.84) \text{ kJ/mol}^{(18)} \\ &n\text{H}_2\text{O}_{(1,25^\circ\text{C})} \rightarrow n\text{H}_2\text{O}_{(\text{g},700^\circ\text{C})} = n \cdot \Delta H_4 = n \cdot (69.0 \pm 0.1) \text{ kJ/mol}^{(15)} \\ &m\text{CaO} \cdot 1/2\text{Mn}_2\text{O}_3 \cdot 1/4y\text{O}_2 \cdot n\text{H}_2\text{O}_{(\text{s},25^\circ\text{C})} \rightarrow \left[ m\text{CaO} + 1/2\text{Mn}_2\text{O}_3 \right]_{(\text{sln},700^\circ\text{C})} + \left[ n\text{H}_2\text{O} + 1/4y\text{O}_2 \right]_{(\text{g},700^\circ\text{C})} \\ &= \Delta H_5 = \Delta H_{\text{ds}} \text{ sample kJ/mol} \\ &\left[ m\text{CaO} + 1/2\text{Mn}_2\text{O}_3 \right]_{(\text{s},25^\circ\text{C})} + 1/4y\text{O}_2(\text{g},25^\circ\text{C}) + n\text{H}_2\text{O}_{(1,25^\circ\text{C})} \rightarrow m\text{CaO} \cdot 1/2\text{Mn}_2\text{O}_3 \cdot 1/4y\text{O}_2 \cdot n\text{H}_2\text{O}_{(\text{s},25^\circ\text{C})} \\ &= \Delta H_{\text{f-ox}}^* \text{ kJ/mol} \end{aligned}$$

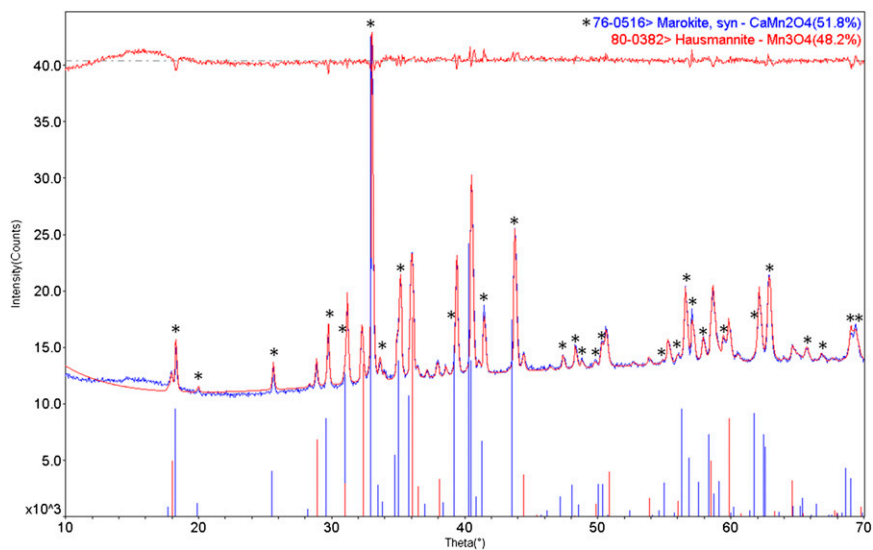
**Enthalpy of formation from the elements.** Enthalpy of formation from the elements,  $\Delta H_f^\circ$ , of the CaMnO layer structure phases from the elements was calculated by adding the appropriate enthalpies

of formation of the binary oxides from the elements, multiplied by the stoichiometric coefficients in the formation reactions. The values for binary oxides are listed below (Table S1).

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**Fig. S1.** Typical X-ray diffraction (XRD) pattern of a layered structure CaMnO material before heating to 1,000 °C. The two broad peaks are consistent with a layered structure. The small sharp peak is a silicon diffraction peak coming from a scratch in the zero-background sample holder.



**Fig. S2.** Typical XRD pattern of CaMnO after heating to 1,000 °C. The scan line in the middle of the figure is the actual measured pattern and the overlay is the calculated pattern, as measured with whole-pattern profile fitting performed using Jade software (version 6.11, 2002). Additionally, as calculated with the Jade software package, the scan line in the upper part of the figure is the computed difference pattern and represents the difference between observed and theoretical intensities, whereas the lines in the lower part of the figure correspond to reference peak positions for marokite (with \*) and hausmannite (without \*). The compositions of the two mineral oxide phases, reported at the top of the figure as wt%, are 48.2% hausmannite and 51.8% marokite. syn, synthetic.



**Fig. S3.** Transmission electron microscopy (TEM) image of CaMnO shows layered structure morphology.

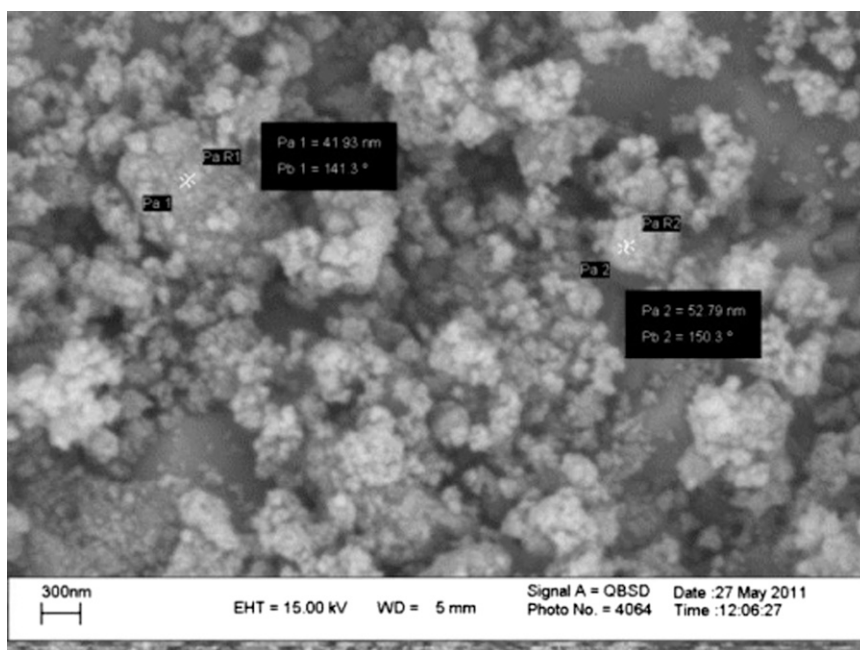


Fig. S4. SEM image shows that the CaMnO samples consist of aggregates of fundamental nanoscale particles (Pa) from 20 to 60 nm (or below 100 nm) in size. EHT, electron high tension; QBSD, quadrant back scattering detector; WD, working distance.

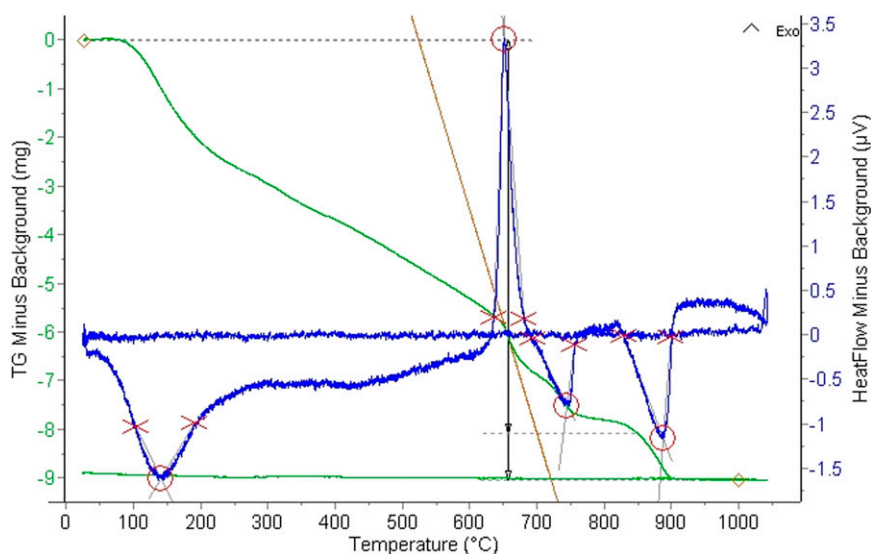


Fig. S5. Thermogravimetric (TG) differential scanning calorimetry (DSC) representative of the CaMnO samples. Analysis of the TG-DSC shows an endotherm for water loss at 142 °C (peak 1) and two additional endotherms at 745 °C (peak 3) and 887 °C (peak 4), which may represent both water and oxygen loss, as well as an exothermic peak at 650 °C (peak 2) possibly caused by sample coarsening. Exo, exothermic (exothermic peak direction in this context); green line, mass loss; blue line, heat flow; brown line, part of calculation for integration of the curve to determine total mass loss for the thermogravimetric analysis; diamonds, initial and final temperature used in the baseline; dotted lines, extrapolation of the baseline, which in the present case is linear due to the background subtraction; "x" marks the selection of the peak (indicated by the circle) and the analysis is used here to identify the temperature of the reported processes in the figure.

**Table S1. Summary of standard formation enthalpies of binary oxides ( $\Delta H_f^\circ$ )**

Oxide	$\Delta H_f^\circ$ , kJ/mol
Mn <sub>2</sub> O <sub>3</sub> (bixbyite)	-959.0 ± 1.0
MnO <sub>2</sub> (pyrolusite)	-520.0 ± 0.7
H <sub>2</sub> O (liquid)	-285.8 ± 0.1
CaO (lime)	-635.1 ± 0.9

Standard formation enthalpies are from a study by Robie and Hemingway (18).