



STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 78 (2022)

Supporting information for article:

Synthesis and structure of high-purity BaCe_{0.25}Mn_{0.75}O₃: an improved material for thermochemical water splitting

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S1. Dehydration of Cerium (III) Carbonate Hydrate

Thermal gravimetric analysis (TGA) in inert N₂ ambient was used to determine dehydration temperature and kinetics of cerium (III) carbonate hydrate ($\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$, Sigma Aldrich 99.9%), as seen in Figure S1. TGA of $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ indicated a mass loss of 22.2% after an isotherm at 150 °C, in keeping with dehydration temperature of 150 °C, approximate initial water content of 3.6 mols H₂O per mol $\text{Ce}_2(\text{CO}_3)_3$, and an onset of decomposition of anhydrous $\text{Ce}_2(\text{CO}_3)_3$ to Ce_2O_3 near 190 °C. Informed by these results, all $\text{Ce}_2(\text{CO}_3)_3$ was first dehydrated in a vacuum oven at approximately 150 °C for 24 hr prior to weighing.

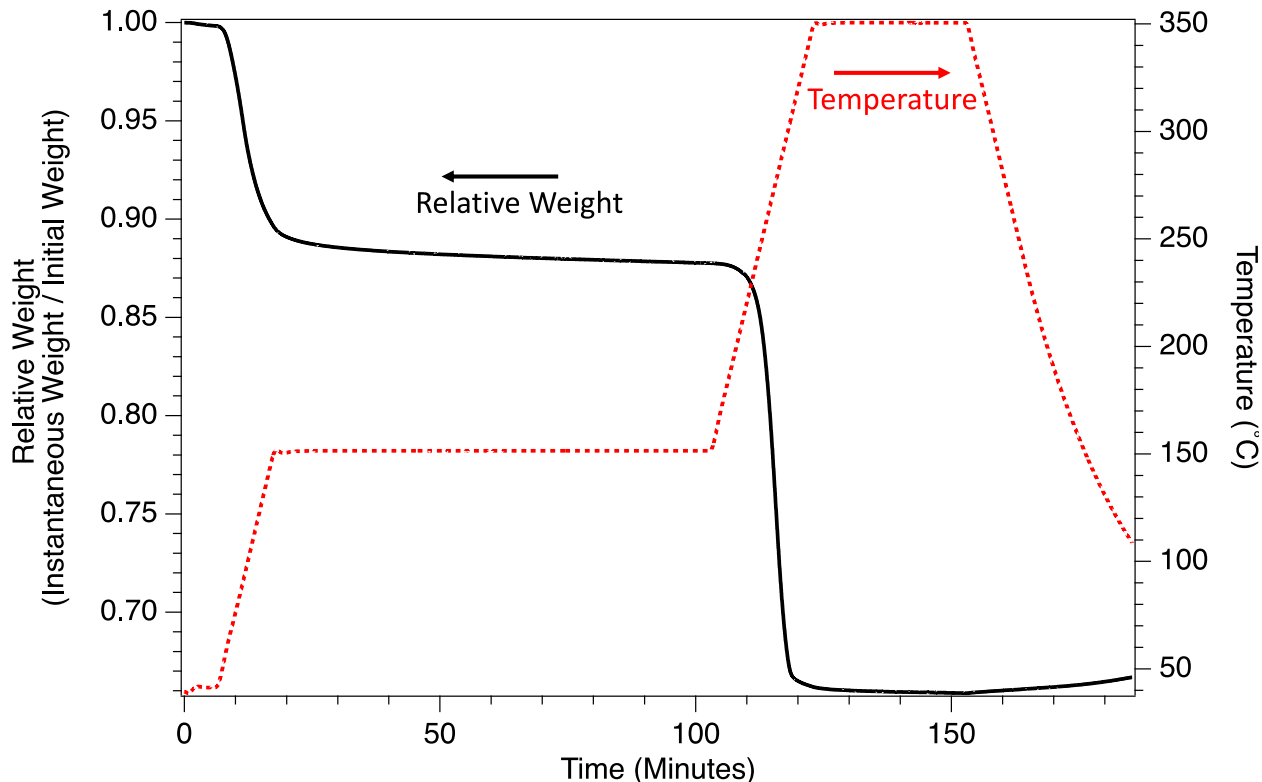


Figure S1 TGA results of initially $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ under inert N₂ gas flow. Results show initial dehydration mass loss during ramp to 150 °C, followed by an isotherm at 150 °C during which the weight

asymptotically approaches a constant value. Subsequent heating to 350°C caused further decomposition as CO₂ evolves.

TGA analysis of sol-gel synthesized 12R-BCM sample heated under ultra-high purity argon gas flow. Data indicate that kinetic limitations inhibit bulk reduction of 12R-BCM below 850°C. These results support that bulk oxidation state was unlikely to change during $\leq 700^\circ\text{C}$ in-situ vacuum XRD despite slower heating rates during XRD.

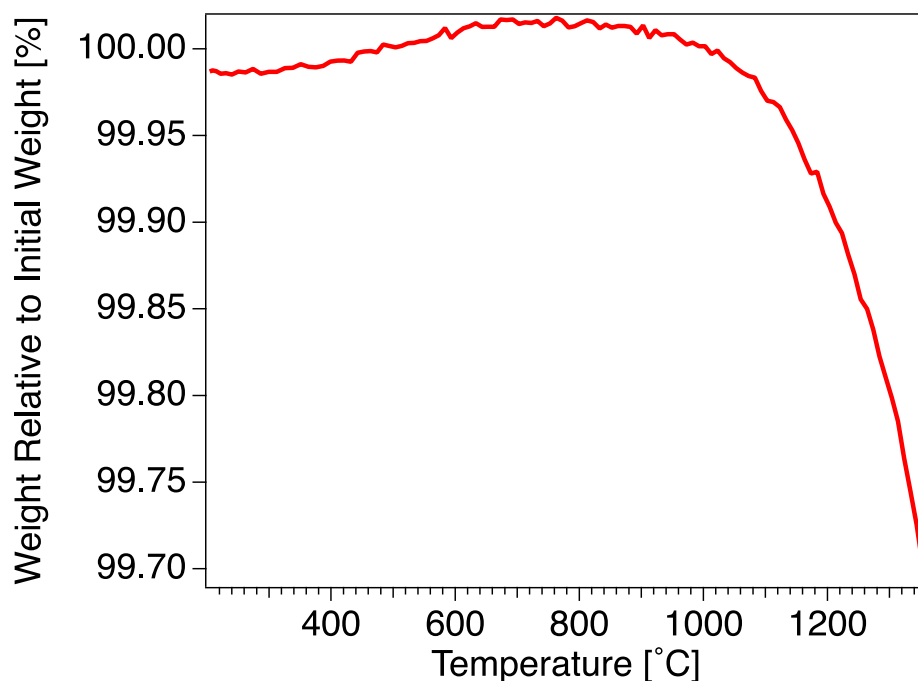


Figure S2 TGA results of heating 12R-Ba₄CeMn₃O₁₂ under ultra-high purity argon gas flow, at constant heating rate of 20 K/min. Results demonstrate relative kinetic stability of material until temperatures >900°C. Mass is normalized to initial room temperature mass, with variations below 850°C beneath sensitivity limits.

S2. RBS Edge-Fitting

Analysis of the RBS data from BCM was done using only the front edge of each elemental step, which corresponds to only the top few nanometers of the powder. The sample BCM powder was from the sample sol-gel synthesized and annealed at 1450 °C, and the sample was sprinkled and lightly tapped onto carbon tape affixed to the sample holder. To determine the step heights in the RBS data (Figure S2), the

average of 10 points directly before (higher energy than) the step was taken and subtracted from the average of the 10 points right after (lower energy, with the increased normalized intensity) the step for both Mn and the joint Ba/Ce signals. The standard deviation of the calculated edge height was determined by adding the squares of the standard deviations determined from the regions before and after the step edges, then taking the square root of that sum to ensure propagation of error was accounted for.

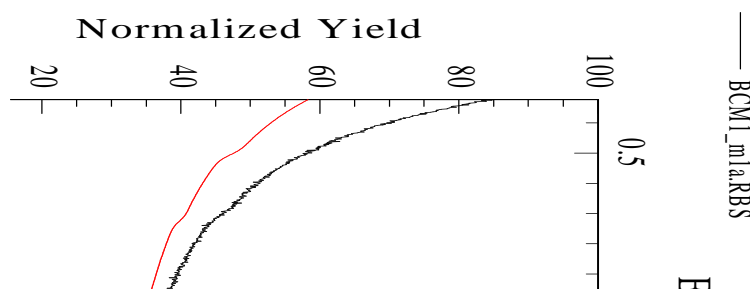


Figure S3 RBS data for the BCM Sol-gel sample annealed at 1450°C. Raw data is shown in black, and the initial by-hand fit using thin-film model is in red. Due to the surface roughness and exposed regions of Carbon tape between the grains of powder, the thin-film model deviates substantially from the raw data, hence the use of the surface analysis method for determining cation stoichiometries.

Scattering cross-sections for each element were determined using the following equation:

$$\sigma_x = 5.1837E6 * \left(\frac{Z_1 Z_2}{E[keV]} \right)^2 * \frac{\left(\sqrt{(M_2^2 - M_1^2(\sin \theta)^2)} + M_2 \cos \theta \right)^2}{M_2(\sin \theta)^4 \sqrt{M_2^2 - M_1^2(\sin \theta)^2}}$$

in which σ_x is the Rutherford backscattering cross-section of element X in millibarn per steradian (mb/sr), Z_1 and M_1 are the nuclear charge and the mass of the projectile respectively, in this case for the He ion beam, $Z_1 = 2$ and $M_1 = 4$, Z_2 and M_2 are the nuclear charge and mass of the target atom, respectively, and

θ is the scattering angle. E is the energy of the incident He ion, which in this case is 2000 keV. (Mayer, 2003)

The scattering cross-sections of the Ba, Ce, and Mn were then used, along with the edge heights from the raw RBS data, to determine the relative amounts of each element. Since Barium and Cerium are too close together in atomic number to differentiate between them with the RBS setup used, the model used assumed the anticipated ratio of 4 Ba for every 1 Ce to model a convoluted step with contributions from both elements. The total edge height was split into the constituent amounts, accounting for the relative scattering cross-sections by the equations:

$$EdgeHeight_{Ba} = \frac{4 * EdgeHeight_{Combined} * \sigma_{Ba}}{4\sigma_{Ba} + \sigma_{Ce}}$$

and

$$EdgeHeight_{Ce} = \frac{EdgeHeight_{Combined} * \sigma_{Ce}}{4\sigma_{Ba} + \sigma_{Ce}}$$

in which $EdgeHeight_x$ is the edge height of X, whether it be Ba, Ce, or the combined edge height as determined from the raw RBS data. The standard deviations for both elements were calculated in a similar manner, with substituting in the combined standard deviation for the combined edge height. Relative elemental densities (N_x) for each element in the material were determined by taking the calculated edge heights and dividing those by the scattering cross sections, and the cation atomic fractions were determined by dividing the relative elemental density value of the cation of interest by the sum of the elemental densities calculated for each of the cations. The equation for this calculation for Manganese is given by Equation 5 in the main text of the manuscript.

Table S1 Specifics of edge heights and element-specific fitting of Rutherford Backscattering Spectrometry results for 12R-BCM.

Element, X =	Mn	Ba+Ce	Ba	Ce
σ_x [mbarn/sr]	819.388	-	4147.45	4449.28
EdgeHeight _x [counts]	1616	12452	9818.6893	2633.3107
Std. Dev. EdgeHeight _x [counts]	157	133	104.98258	28.1556674
N_x [counts·sr/mbarn]	1.97220364	-	2.3674039	0.59185097
Std. Dev. N_x [counts·sr/mbarn]	0.19107483	-	0.02531256	0.00632814

Cation At. Frac.	0.39992299	-	0.48006161	0.1200154
Std. Dev. At. Frac.	0.02310685	-	0.01364026	0.00341006
Cation At. %	40.0%	-	48.0%	12.0%
Std. Dev. Cation At. %	2.3%	-	1.4%	0.3%

S3. Scanning Electron Microscopy of Related 12R BCM materials

Electron microscopy techniques were used to investigate local stoichiometry of a different batch of modified Pechini method BCM than that used in the main text. This second batch of BCM was synthesized under matching conditions to the modified Pechini used in the main text, but was not as extensively characterized with XRD. However, the local stoichiometry and uniformity apparent in this second batch is added confirmation of the local homogeneity in these 12R-BCM samples.

Pieces of pressed pellets were mounted onto Al stubs with double-sided C tape and investigated with a ThermoFisher Apreo Lo Vac Scanning Electron Microscope (SEM). A Bruker Quantax system with a 60 mm² active detector area was used for compositional measurements with energy dispersive spectroscopy (EDS). Spectrum image maps were collected over areas of several hundreds of square microns at an accelerating voltage of 15 kV. Pixel dwell times were 16 μ sec for 1536x1033 pixel frames and multiple frames were collected with drift correction applied between each frame until the sum spectrum contained a few tens of millions of counts. A standardless quantification ZAF routine (Goldstein *et al.*, 2003) was used in the Bruker Espirit software to estimate the composition and relative stoichiometry of the pellet based on the sum spectrum collected from the entire mapped region. These results are shown in Figure S3. SEM-EDS results of the 12R-BCM phase yielded atomic percentages for Ba at 51.6% \pm 1.85%, Ce at 12.7% \pm 0.5%, and Mn at 35.8% \pm 1.7%.

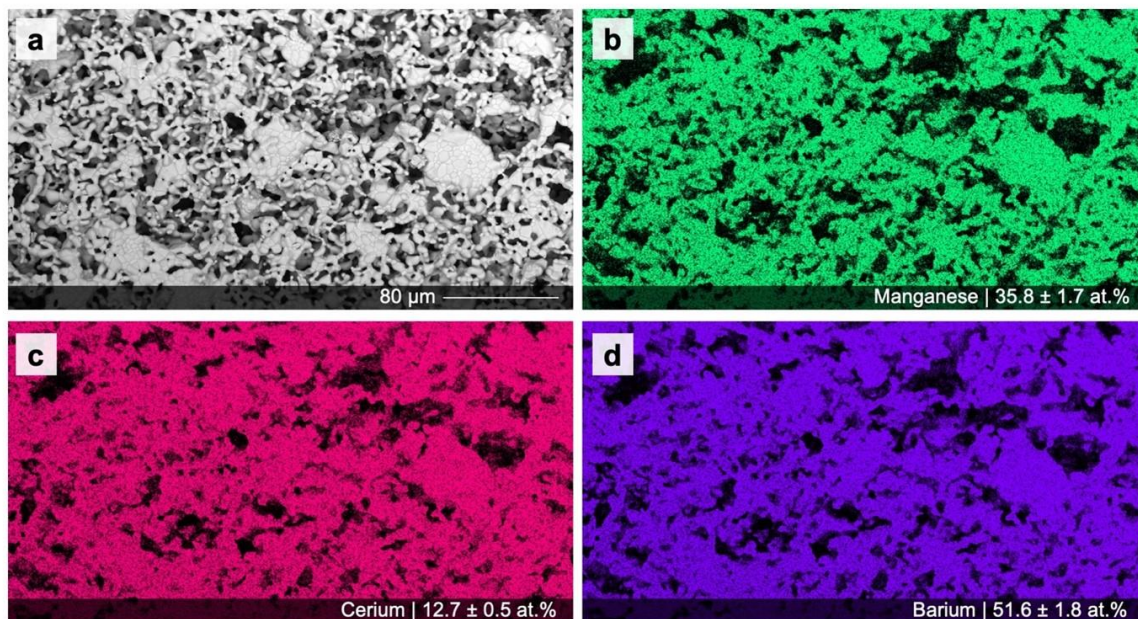


Figure S4 (a) SEM micrograph of BCM synthesized by the solid-state method annealed at 1500 °C. (b-d) EDS maps illustrating Mn, Ce, and Ba, uniformly distributed at the micron length scale.