

Supporting Information

Two-dimensional charge disproportionation of the unusual high valence state Fe^{4+} in a layered double perovskite

Yoshiteru Hosaka[†], Noriya Ichikawa[†], Takashi Saito[†], Pascal Manuel[‡], Dmitry Khalyavin[‡], J. Paul Attfield[§], Yuichi Shimakawa^{**†, †}

[†]*Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

[‡]*ISIS, Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, United Kingdom*

[§]*Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom*

[†]*Japan Science and Technology Agency, CREST, Uji, Kyoto 611-0011, Japan*

This supporting information includes 3 figures and 2 tables.

e-mail: shimak@scl.kyoto-u.ac.jp

(1) Sample preparation and characterization

The precursor compound, $\text{Ca}_2\text{FeMnO}_5$, was prepared by conventional solid-phase reaction. Stoichiometric amounts of CaCO_3 , Fe_2O_3 , and MnCO_3 were well mixed, calcined at 1000 °C in air, ground, and fired at 1250 °C in air. Pellets of the calcined powder sample were then fired at 1100 °C in vacuum. The prepared $\text{Ca}_2\text{FeMnO}_5$ was treated at 200 °C for 6 hours in flowing ozone-containing oxygen.

The result of the crystal structure analysis and the selected bond distances and angles calculated for from the refined structural parameters for $\text{Ca}_2\text{FeMnO}_6$ are given below. The layered arrangement of the *B*-site Fe/Mn cations was also confirmed in high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) combined with electron energy loss spectroscopy (EELS). Oxygen content of the sample was estimated by measuring the change in the sample weight during thermogravimetric (TG) analysis. See reference [1] for the details.

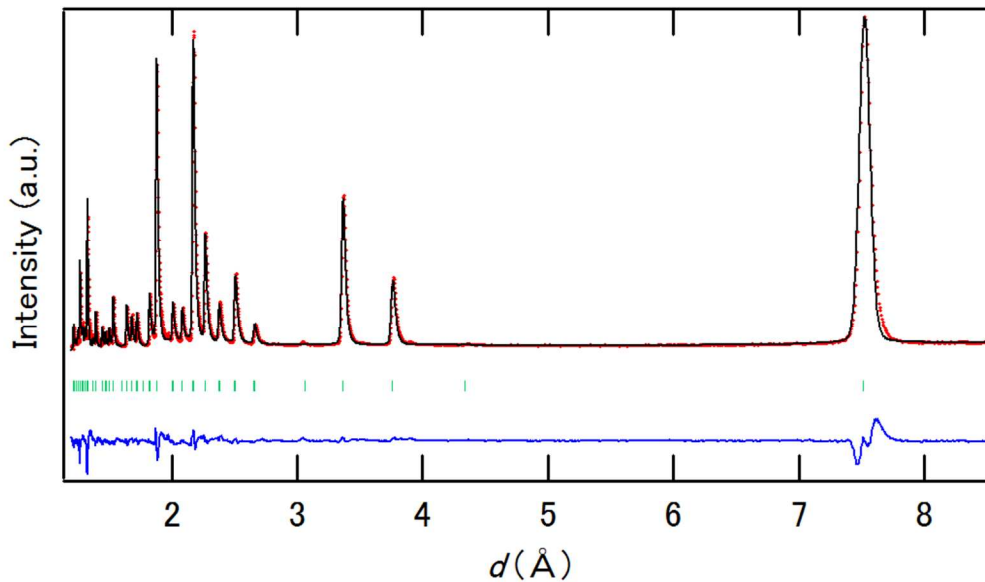


Figure SI 1. Results of the Rietveld refinements of neutron diffraction data for $\text{Ca}_2\text{FeMnO}_6$ at room temperature. The dots and solid line represent observed and calculated patterns, respectively. The plot below the diffraction pattern is the difference between the observed and calculated intensities. Vertical marks below the profiles are Bragg reflection positions.

Table SI 1. The refined structure parameters obtained with neutron diffraction data for $\text{Ca}_2\text{FeMnO}_6$ at room temperature. Space group; $P2_1/c$, $a = 7.5077(4)$ Å, $b = 5.3055(2)$ Å, $c = 5.3217(3)$ Å, and $\beta = 90.00(1)^\circ$. $R_{\text{WP}} = 4.69\%$.

Atom	x	y	z	B (Å ²)	Occupancy
Ca	0.2540(7)	0.503(2)	0.529(2)	1.2(1)	1.0
Fe/Mn	0.0	0.5	0.0	1.0(1)	0.922(4)/0.078
Mn/Fe	0.5	0.5	0.0	1.6(4)	0.856(2)/0.144
O1	0.2497(7)	0.060(1)	0.493(1)	1.0(1)	1.0
O2	0.032(1)	0.712(2)	0.286(2)	2.0(2)	1.0
O3	0.5354(9)	0.286(2)	0.716(2)	1.7(1)	1.0

Table SI 2. The selected bond distances and angles for $\text{Ca}_2\text{FeMnO}_6$ determined from the structure analysis with neutron diffraction measured at room temperature.

Fe-O1 (Å)	1.902(6)
Fe-O2 (Å)	1.91(1)
Mn-O3 (Å)	1.92(1)
Mn-O1 (Å)	1.907(6)
Fe-O2-Fe ($^\circ$)	157.8(3)
Fe-O1-Mn ($^\circ$)	160.5(3)
Mn-O3-Mn ($^\circ$)	157.4(1)

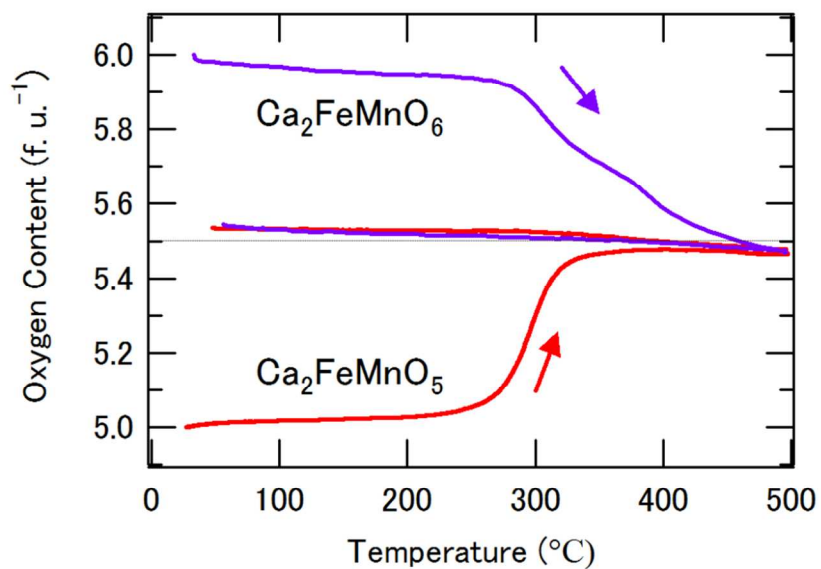


Figure SI 2. Changes in oxygen content during TG measurements of $\text{Ca}_2\text{FeMnO}_6$ (blue) and the precursor brownmillerite $\text{Ca}_2\text{FeMnO}_5$ (red) in air. These changes in oxygen content were calculated from the observed weight changes. The final products after the TG measurements were identical, and the chemical composition of the product was $\text{Ca}_2\text{FeMnO}_{5.5}$.

(2) Resistivity measurement

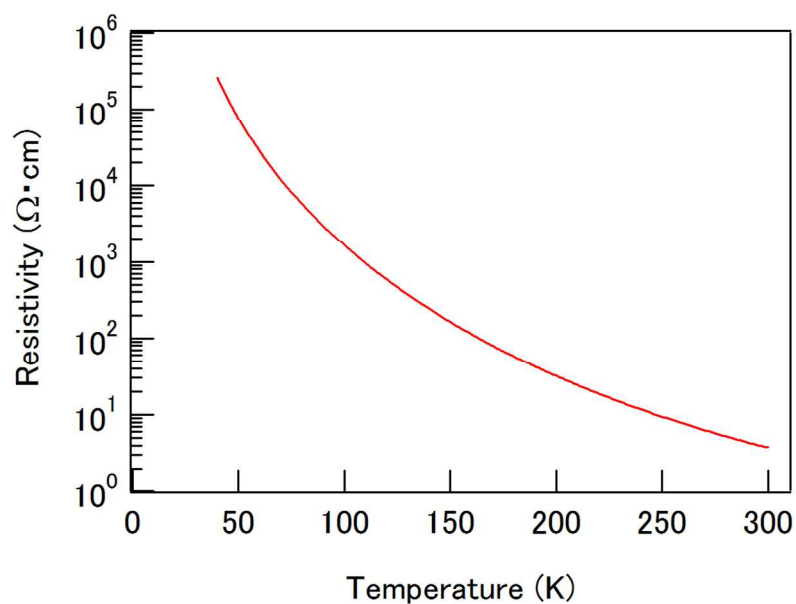


Figure SI 3. Temperature dependence of resistivity for $\text{Ca}_2\text{FeMnO}_6$ (measured resistivity of a pressed powder pellet). No anomaly was observed at the charge disproportionation transition temperature around 200 K.

Reference

- (1) Hosaka, Y.; Ichikawa, N.; Saito, T.; Haruta, M.; Kimoto, K.; Kurata, H.; Shimakawa, Y. *Bull. Chem. Soc. Jpn.* **2015**, 88, 657.