Electronic Supplementary Information (ESI)

Redox characteristics variations in the cation-ordered perovskite oxides $BaLnMn_2O_{5+\delta}$ (Ln = Y, Gd, Nd, and La) and $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ ($0 \leq x \leq 1$)

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(1) XRD patterns for as-synthesized Ba*Ln*$Mn_2O_{5+\delta}$ with *Ln* = Y, Gd, Nd, and La.

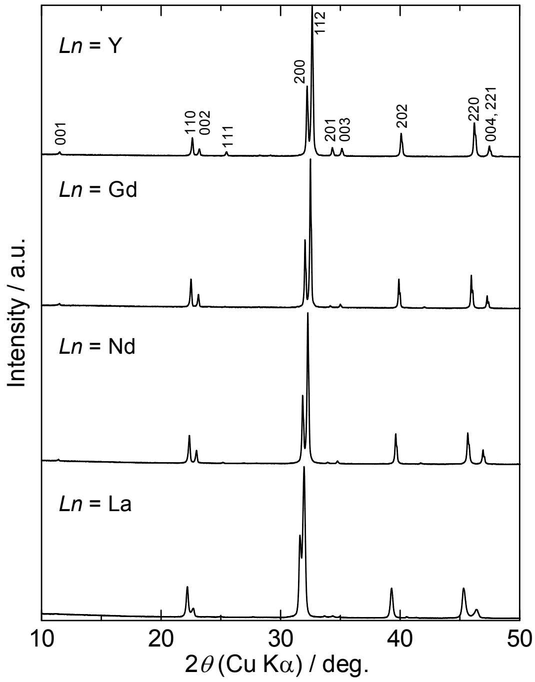

Fig. S1. X-ray powder diffraction patterns for the as-synthesized Ba*Ln*$Mn_2O_{5+\delta}$ products with *Ln* = Y, Gd, Nd, and La.

(2) SEM images of the Ba*Ln*$Mn_2O_{5+\delta}$ products.

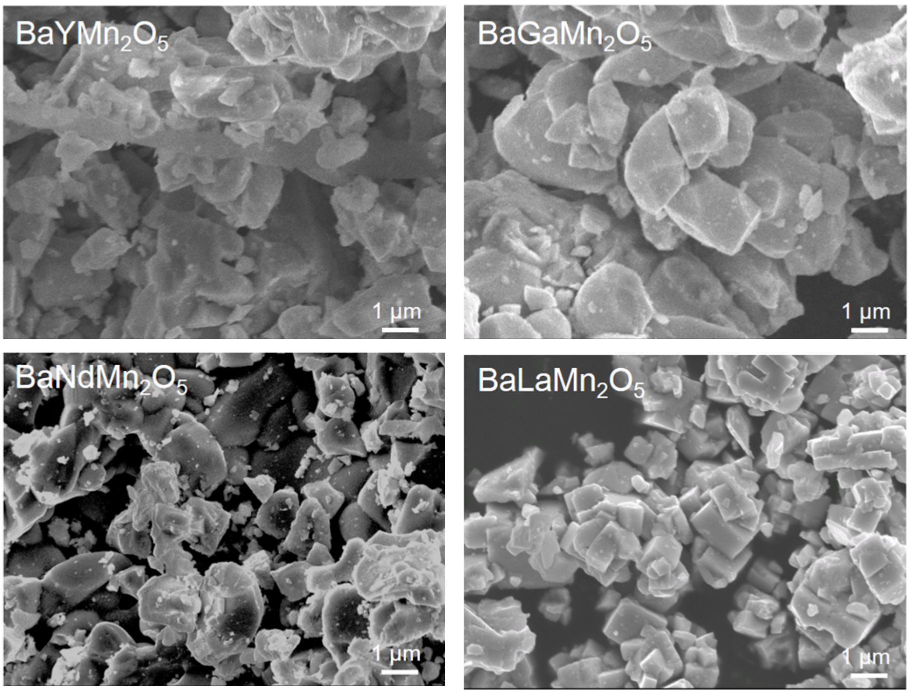

Fig. S2. SEM images of the Ba*Ln*$Mn_2O_{5+\delta}$ products: upper left, *Ln* = Y; upper right, *Ln* = Gd; lower left, *Ln* = Nd; lower right, *Ln* = La.

(3) XRD patterns for as-synthesized $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ with x = 0, 0.1, 0.3, 0.5, and 1.

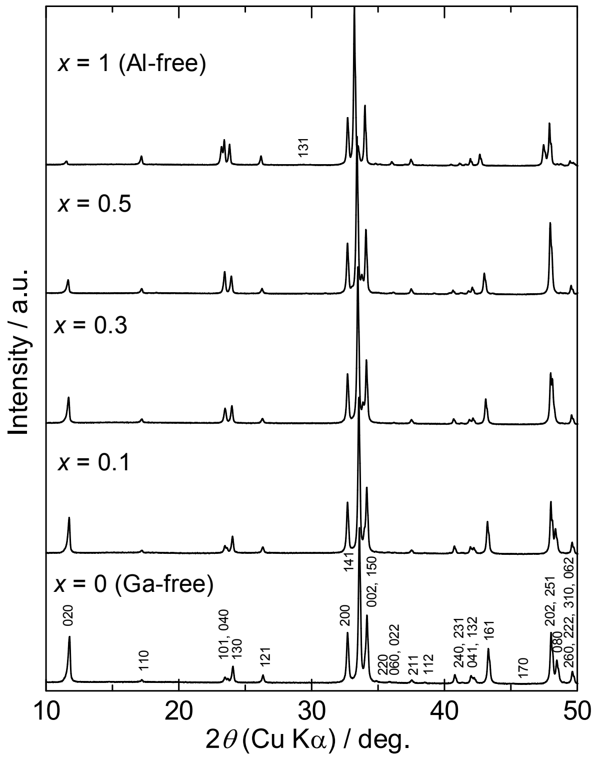

Fig. S3. X-ray powder diffraction patterns for the as-synthesized $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ products with x = 0, 0.1, 0.3, 0.5, and 1.

The $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ system was previously investigated by Antipov and coworkers.[22-25] They focused on a detailed structural feature regarding the ordering pattern of the two mirror-related tetrahedral $(Al,Ga)O_4$ chains, arbitrarily called "L" and "R". The $Ca_2GaMnO_{5+\delta}$ (x = 1) end member is found to contain alternate stacking of L/R-chain layers with partial intermixing of the L/R chains, resulting in a primitive unit cell (space group *Pcmn*).[24] A decrease in the Ga content (x) leads to disrupted L/R-chain ordering, and eventually a complete phase transformation at $x < 0.5$, where the crystal lattice is described with a body-centered unit cell (space group *Ibm*2). For our sample series, the 131 diffraction peak ($2\theta \approx 29°$), which can be used as an indicator of the L/R-chain ordering, is visible for x = 1 and absent for x = 0, in agreement with the report of Antipov and coworkers.[24] Meanwhile, this peak is hardly seen also for x = 0.5 contrary to their report, suggesting that the critical composition for the phase transformation would depend on the synthesis condition. It is likely that the L/R-chain ordering would play a negligible role in the oxygen intake/release characteristics, and we do not discuss its influence.

(4) Plots of the orthorhombic *a*-, *b*-, and *c*-axis lengths for $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ with respect to the Ga content (*x*).

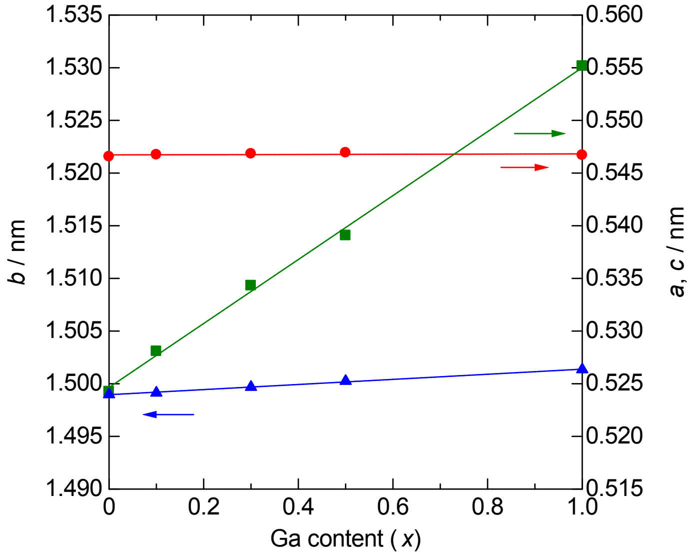

Fig. S4. The orthorhombic *a*-, *b*-, and *c*-axis lengths for the as-synthesized $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ with respect to the Ga content (*x*).

(5) SEM images of the $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ products.

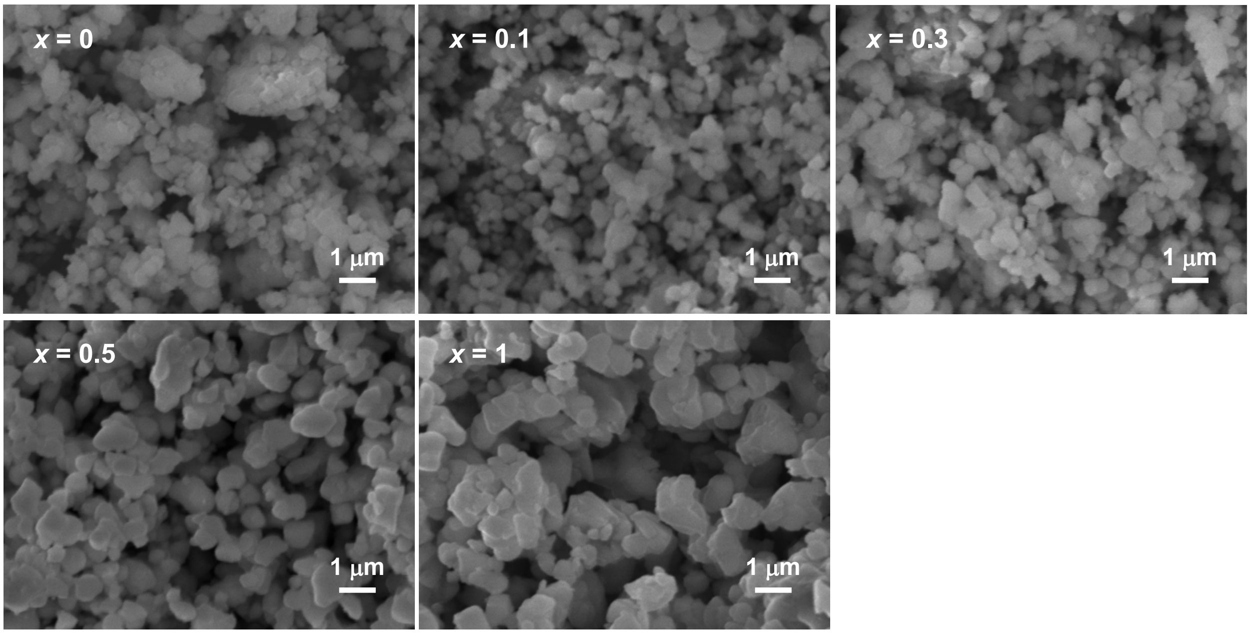

Fig. S5. SEM images of the $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ products: upper left, $x = 0$; upper middle, $x = 0.1$; upper right, $x = 0.3$; lower left, $x = 0.5$; lower middle, $x = 1$.

(6) XRD patterns for the oxygenated $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ products.

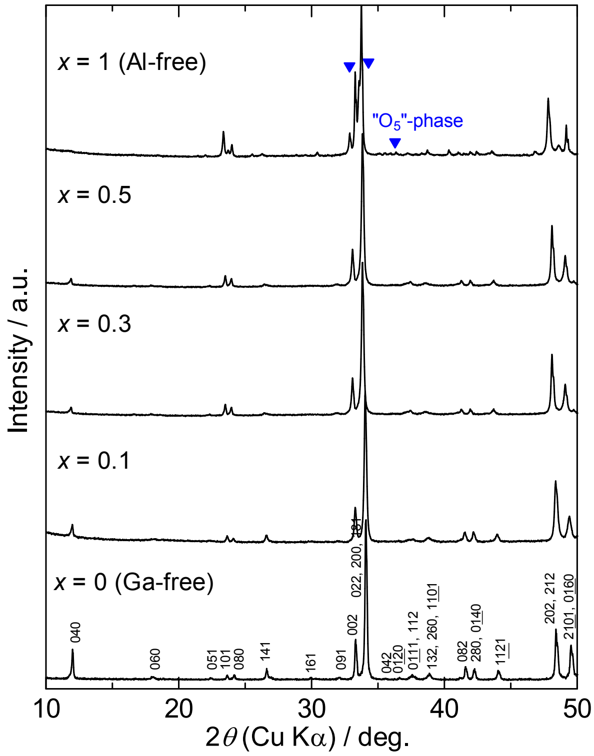

Fig. S6. X-ray powder diffraction patterns for the oxygenated $Ca_2Al_{1-x}Ga_xMnO_{5+\delta}$ products with x = 0, 0.1, 0.3, 0.5, and 1. For x = 1, diffraction peaks of the oxygen-stoichiometric "O_5" phase are marked with blue triangles.