Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY INFORMATIONS

Tuning the Mn valence state in new $Ca_{0.66}Mn_{2-x}Al_xO_4$ ($x \leq 0.4$) oxides: impact on magnetic and redox properties.

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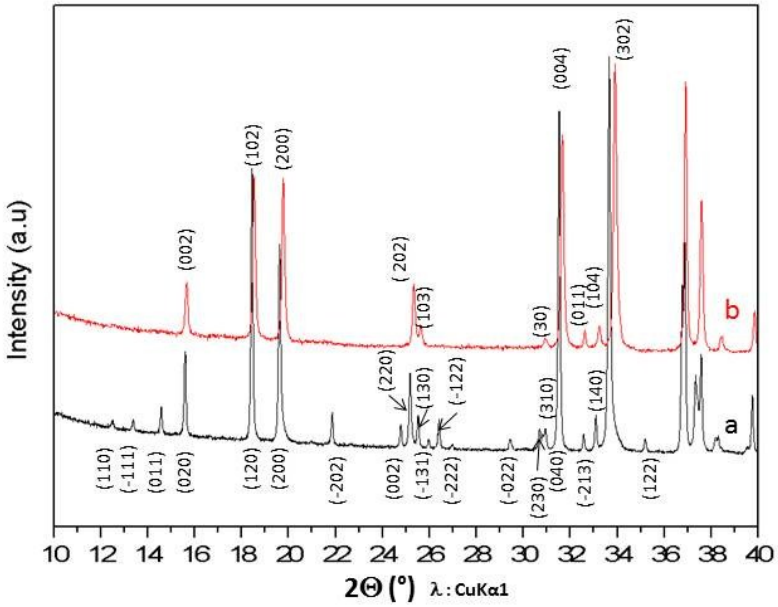

Figure S1: X-ray powder diffraction patterns 10°-40° 2Θ range (counting time 2000s per step: 0.008°) of a) $CaMn_3O_6$=$Ca_{0.66}Mn_2O_4$ (monoclinic unit cell, SG: $P2_1/a$) and b) $Ca_{0.66}Mn_{1.6}Al_{0.4}O_4$ (orthorhombic unit cell, SG: Pnma) compounds. (hkl) indexations at low 2Θ angles are mentioned.

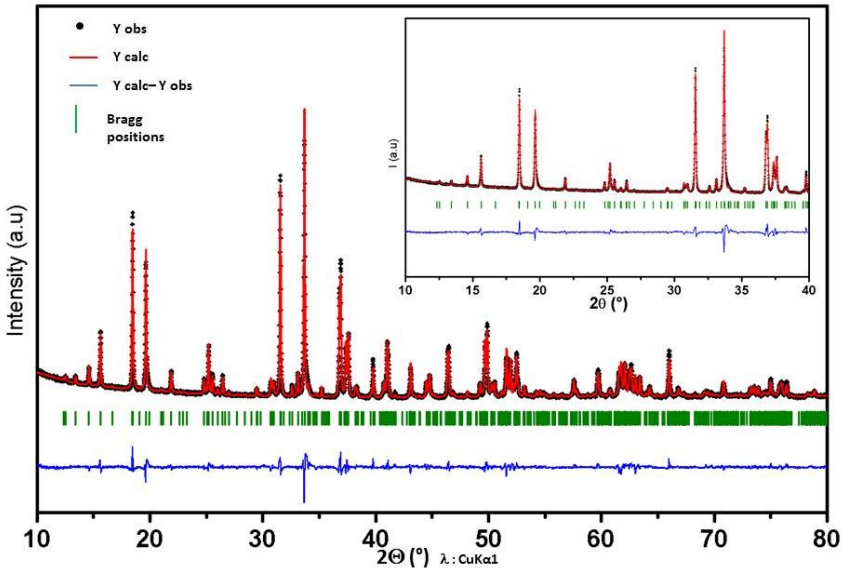

Figure S2: Rietveld refinement of X-ray powder diffraction patterns (10°-80° 2Θ range, counting time 2000s per step: 0.008°) of $CaMn_3O_6$=$Ca_{0.66}Mn_2O_4$ compound. Calculated (in red), observed (in black), difference (in blue) patterns are represented. Bragg peaks (in green) are noted.

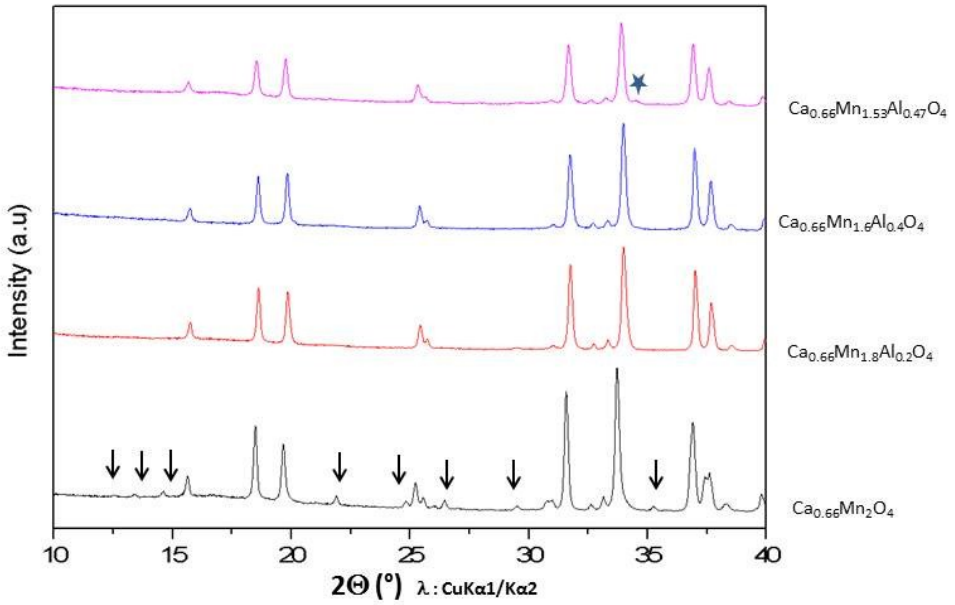

Figure S3: X-ray powder diffraction patterns (10°-40° 2Θ range, counting time 500s per step: 0.017°) of $Ca_{0,66}Mn_{2-x}Al_xO_4$ ($0<x\leq0.47$) compounds. For x=0.47, the impurity (Brownmillerite-type phase) is marked with a star.

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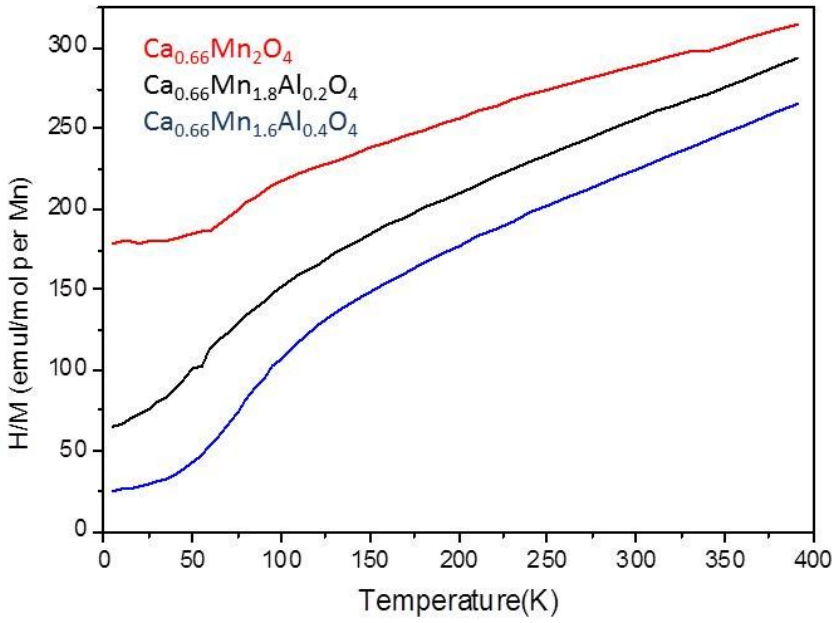

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Figure S4: Comparison of the temperature dependence of H/M susceptibility curve per mole of Mn for $Ca_{0.66}Mn_2O_4$ (in red) , $Ca_{0,66}Mn_{1,8}Al_{0,2}O_4$ (in black) and $Ca_{0,66}Mn_{1,6}Al_{0,4}O_4$ (in blue) compounds (recorded with a magnetic field of 10 KOe).

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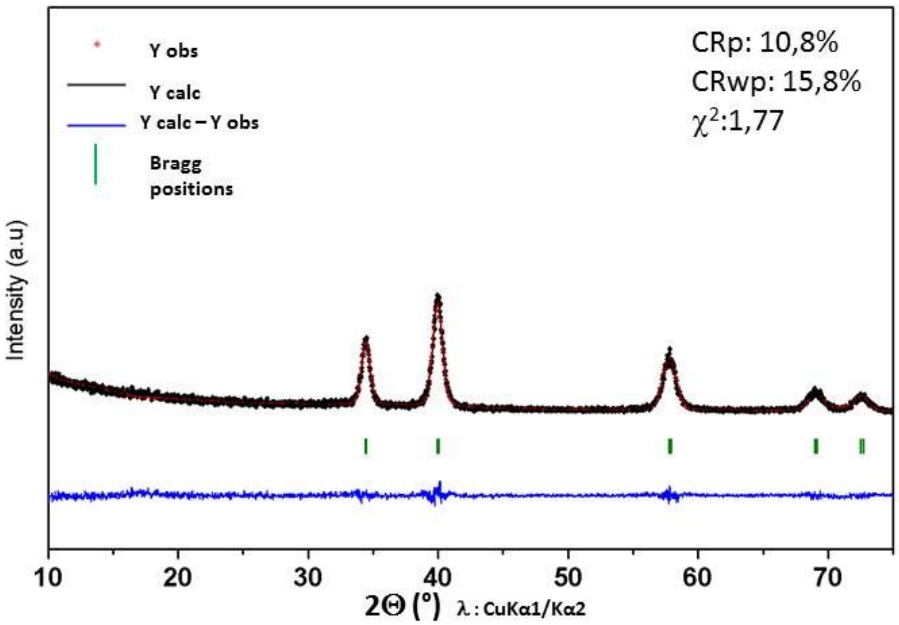

Figure S5: Full Pattern Profile refinement of X-ray powder diffraction patterns (10°-75° 2Θ range, counting time 60 s per step : 0.017°) of the $Ca_{0.23}Mn_{0.56}Al_{0.14}O$ compound (rocksalt-type structure) obtained after reduction under Ar/H_2 5% of $Ca_{0.66}Mn_{1.6}Al_{0.4}O_4$ oxide (TGA-Figures 9 and 12)

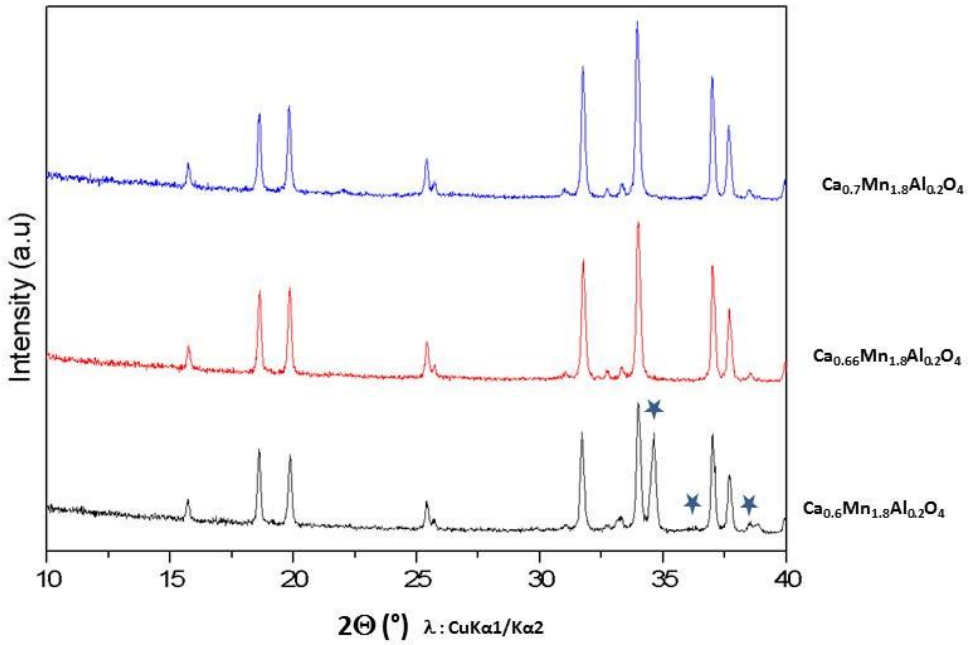

Figure S6 X-ray powder diffraction patterns (10°-40° 2Θ range, counting time 500s per step: 0.017°) of a) $Ca_{0,6}Mn_{1,8}Al_{0,2}O_4$, b) $Ca_{0,66}Mn_{1,8}Al_{0,2}O_4$ and c) $Ca_{0,7}Mn_{1,8}Al_{0,2}O_4$ compounds. For the composition $Ca_{0,6}Mn_{1,8}Al_{0,2}O_4$ the impurity considered as Brownmillerite-type (SG:Imma) phase ($Ca_2(Mn,Al)_2O_5$) is marked with a star.

Atom	Wyckoff positions	x	y	z	Biso [Å^3]	Occupancy
Ca1	4e	0.2476(6)	0.3337(6)	0.5585(7)	1.72(7)	1
Ca2	4e	0.2429(6)	0.3353(6)	0.9361(7)	1.72(7)	1
Mn1	4e	0.0517(5)	0.1150(4)	0.4619(7)	0.37(3)	1
Mn2	4e	0.4225(6)	0.6143(4)	0.8683(8)	0.37(3)	1
Mn3	4e	0.0871(6)	0.5967(4)	0.4737(7)	0.37(3)	1
Mn4	4e	0.4058(6)	0.0938(5)	0.8582(7)	0.37(3)	1
Mn5	4e	0.0708(6)	0.1036(4)	0.7982(8)	0.37(3)	1
Mn6	4e	0.0788(5)	0.5939(5)	0.8022(8)	0.37(3)	1
O1	4e	0.301(1)	0.642(1)	0.599(1)	0.61(5)	1
O2	4e	0.196(1)	0.161(1)	0.714(2)	0.61(5)	1
O3	4e	0.385(2)	0.977(1)	0.677(3)	0.61(5)	1
O4	4e	0.104(1)	0.472(1)	0.666(2)	0.61(5)	1
O5	4e	0.455(1)	0.1986(1)	0.720(3)	0.61(5)	1
O6	4e	0.002(1)	0.691(1)	0.589(2)	0.61(5)	1
O7	4e	0.077(2)	0.910(1)	0.486(2)	0.61(5)	1
O8	4e	0.426(2)	0.417(1)	0.862(3)	0.61(5)	1
O9	4e	0.266(1)	0.644(1)	0.926(2)	0.61(5)	1
O10	4e	0.372(1)	0.991(1)	0.005(3)	0.61(5)	1
O11	4e	0.465(2)	0.203(1)	0.072(3)	0.61(5)	1
O12	4e	0.071(2)	0.909(1)	0.819(3)	0.61(5)	1
Cell parameters SG: P21/a a(Å) b(Å) c(Å) V(Å^3) 10.6879(1) 11.3311(1) 8.4868(1) 868.36(1)						
CRp :20,2% CRwp:19,3 % RBragg=6,09%						

Table S1 : Atomic positions and unit cell unit parameters determined by Rietveld refinement (λCu Kα1, counting time 2000s per step: 0.008°, Figure 4a) of powder X-Ray diffraction data of $CaMn_3O_6$ oxide. The reliability factors CRp, CRpw and RBragg are mentioned.

Atom	Wyckoff positions	x	y	z	Biso [Å^3]	Occupancy
Ca1	4c	0.2452(3)	1/4	0.3335(2)	3.79(8)	0.666
Mn1	4c	0.0705(1)	1/4	0.11139(9)	0.323(1)	0.846(1)
Al1	4c	0.0705(1)	1/4	0.11139(9)	0.323(1)	0.154(1)
Mn2	4c	0.0828(2)	1/4	0.5942(1)	0.323(1)	0.754(1)
Al2	4c	0.0828(2)	1/4	0.5942(1)	0.323(1)	0.246 (1)
O1	4c	0.2900(5)	1/4	0.6512(3)	1.01(4)	1
O2	4c	0.3829(4)	1/4	0.9800(3)	1.01(4)	1
O3	4c	0.4764(5)	1/4	0.1985(3)	1.01(4)	1
O4	4c	0.0691(6)	1/4	0.9149(3)	1.01(4)	1

Cell parameters SG: Pnma

a(Å)	b(Å)	c(Å)	V(Å^3)
8.9535(2)	2.82391(9)	11.2802(3)	285.21(1)

CRp :15.7% CRwp:12.6 % RBragg 6.42 %

Table S2a: Atomic positions and unit cell unit parameters determined by Rietveld refinement (λCu Kα1, counting time 2000s per step: 0.008°, Figure 4a) of powder X-Ray diffraction data of $Ca_{0.66}Mn_{1.6}Al_{0.4}O_4$ oxide. The reliability factors CRp, CRpw and RBragg are mentioned. Structural hypothesis: Al atoms distribution in two Mn1/Mn2 sites.

Atom	Wyckoff positions	x	y	z	Biso [Å^3]	Occupancy
Ca1	4c	0.2446(3)	1/4	0.3329(1)	2.68(5)	0.666
Mn1	4c	0.0694(1)	1/4	0.11153(6)	0.34(1)	0.944(1)
Mn2	4c	0.0831(1)	1/4	0.59460(6)	0.34(1)	0.856(1)
Al2	4c	0.0831(1)	1/4	0.59460(6)	0.34(1)	0.144(1)
Al1	4c	0.0694(1)	1/4	0.11153(6)	0.34(1)	0.056(1)
O1	4c	0.2920(3)	1/4	0.6511(2)	0.36(2)	1
O2	4c	0.3832(2)	1/4	0.9796(2)	0.36(2)	1
O3	4c	0.4745(3)	1/4	0.1978(2)	0.36(2)	1
O4	4c	0.0710(4)	1/4	0.9148(2)	0.36(2)	1
Cell parameters SG: Pnma						
a(Å)		b(Å)		c(Å)	V(Å^3)	
8.9660(2)		2.82493(4)		11.2881(2)	285.908(9)	
CRp :15.7%		CRwp:12.9%		RBragg 8.66%		

Table S2b: Atomic positions and unit cell parameters determined by Rietveld refinement (λCu Kα1, counting time 2000s per step: 0.008°, Figure 4b) of powder X-Ray diffraction data of $Ca_{0.66}Mn_{1.8}Al_{0.2}O_4$ oxide .The reliability factors CRp, CRpw and RBragg are mentioned. Structural hypothesis: Al atoms distribution in two Mn1/Mn2 sites.

Atoms		Distance (Å)
Mn2|Al2	O3	1.912(3)
Mn2|Al2	O3	1.912(3)
Mn2|Al2	O2	1.935(3)
Mn2|Al2	O2	1.935(3)
Mn2|Al2	O1	1.964(5)
Mn2|Al2	O2	1.976(4)
<Mn2-O>		**1.939(3)**
<Δ> = |Mn2-O-<Mn2 -O>|/6		**0.028(3)**
Brown bond valence		**3.70**
Atoms		**Distance (Å)**
Mn1|Al1	O4	1.909(4)
Mn1|Al1	O4	1.909(4)
Mn1|Al1	O1	1.937(3)
Mn1|Al1	O1	1.937(3)
Mn1|Al1	O4	2.215(3)
Mn1|Al1	O3	2.303(4)
<Mn1-O>		**2.035(3)**
<Δ> = |Mn1-O-<Mn1 -O>|/6		**0.153(3)**
Brown bond valence		**3.10**

Atoms		Distance (Å)
Ca1	O4	2.365(5)
Ca1	O4	2.365(5)
Ca1	O3	2.434(5)
Ca1	O2	2.458(4)
Ca1	O2	2.458(4)
Ca1	O1	2.515(4)
Ca1	O1	2.515(4)
Ca1	O3	2.569(5)
<Ca1-O>		**2.460**
<Δ> = |Ca1-O-<Ca1 -O>|/8		**0.054**
Brown bond valence		**2.36**

Table S3a: Bond distances and valence determined from Table S1 (Rietveld refinement of powder X-Ray diffraction data of $Ca_{0.66}Mn_{1.6}Al_{0.4}O_4$, (λCu Kα1, counting time 2000s per step: 0.008°, Figure 4a) oxide. The average <Mn-O> and <Ca-O> bonds distances as well as the average of the difference between main distance and average distance are mentioned. Structural hypothesis: Al atoms distribution in two Mn1/Mn2 sites.

Atoms		Distance (Å)
Mn2|Al2	O3	1.903(2)
Mn2|Al2	O3	1.903(2)
Mn2|Al2	O2	1.941(1)
Mn2|Al2	O2	1.941(1)
Mn2|Al2	O1	1.977(2)
Mn2|Al2	O2	1.979(2)
<Mn2-O>		**1.940(2)**
<Δ> = |Mn2-O-<Mn2 -O>|/6		**0.025(2)**
Brown bond valence		**3.69**
Atoms		**Distance (Å)**
Mn1|Al1	O4	1.915(2)
Mn1|Al1	O4	1.915(2)
Mn1|Al1	O1	1.932(1)
Mn1|Al1	O1	1.932(1)
Mn1|Al1	O4	2.220(2)
Mn1|Al1	O3	2.313(3)
<Mn1-O>		**2.038(2)**
<Δ> = |Mn1-O-<Mn1 -O>|/6		**0.152(2)**
Brown bond valence		**3.09**

Atoms		Distance (Å)
Ca1	O4	2.361(3)
Ca1	O4	2.361(3)
Ca1	O3	2.447(3)
Ca1	O2	2.459(2)
Ca1	O2	2.459(2)
Ca1	O1	2.513(2)
Ca1	O1	2.513(2)
Ca1	O3	2.563(3)
<Ca1-O>		**2.460**
<Δ> = |Ca1-O-<Ca1 -O>|/8		**0.052**
Brown bond valence		**2.14**

Table S3b: Bond distances and valence determined from Table S2a (Rietveld refinement of powder X-Ray diffraction data of $Ca_{0.66}Mn_{1.8}Al_{0.2}O_4$ (λCu Kα1, counting time 2000s per step: 0.008°, Figure 4b) oxide. The average <Mn-O> and <Ca-O> bonds distances as well as the average of the difference between main distance and average distance are mentioned. Structural hypothesis: Al atoms distribution in two Mn1/Mn2 sites.