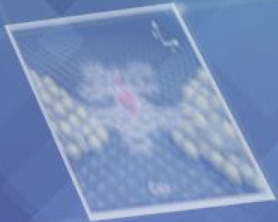
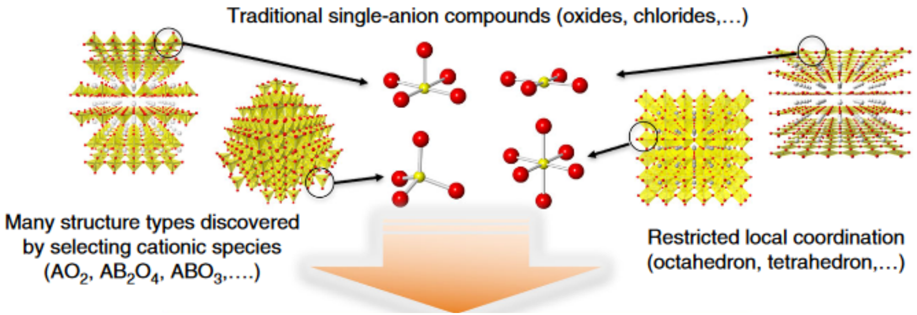


Ca_2MnO_3X (X = Cl, Br) – Oxyhalides with 1-dimensional ferromagnetic chains of square planar $S = 2$ Mn^{3+}

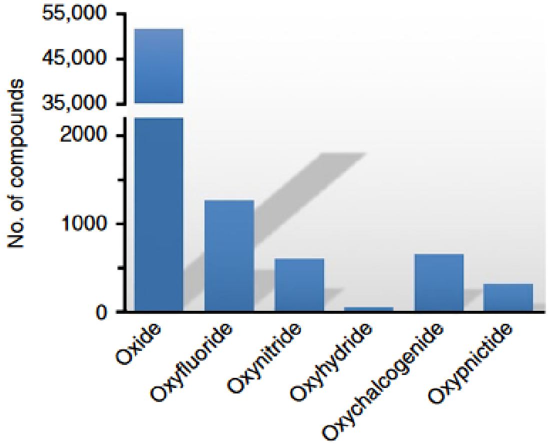
Fabio DENIS ROMERO – 231004

Mixed Anion Materials



Compounds with more than one anionic species

Materials in ICSD:



Kageyama *et al. Nature Communications* 2018

Hume-Rothery rules

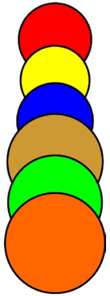
For substitutional solid solutions:

The atomic radius of the solute and solvent atoms must differ by no more than 15%

A significant size difference between ions results in the occupation of different crystallographic sites

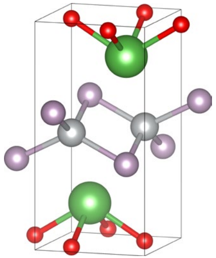
Ionic radii

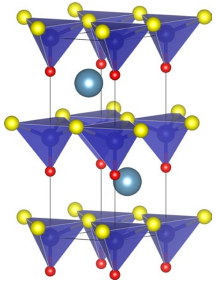
O^{2-}	1.40 Å	
F^{-}	1.33 Å	-5%
N^{3-}	1.46 Å	+4%
S^{2-}	1.84 Å	+31%
Cl^{-}	1.81 Å	+29%
Br^{-}	1.96 Å	+40%

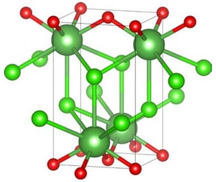


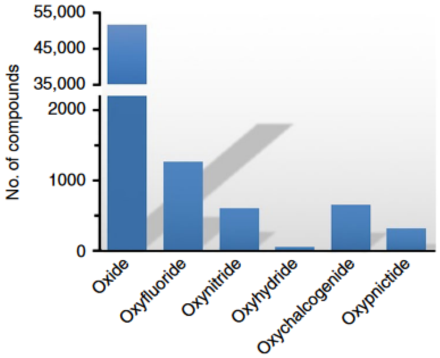
Will favor <u>layered order</u>

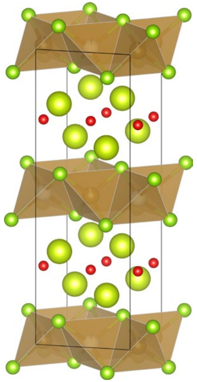
Hume-Rothery and Powell *Zeitschrift für Kristallographie* 1935

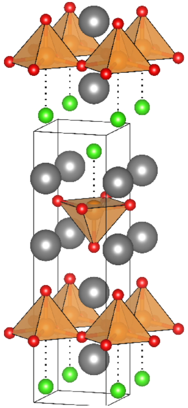

LaNiOP


CaCoOS

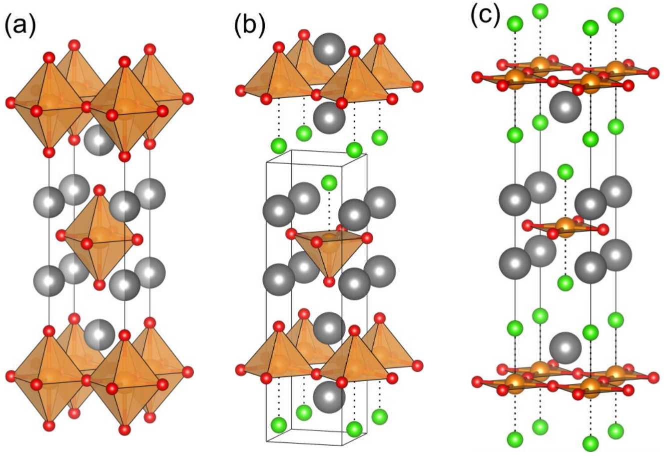

LaOCl




$Ca_2FeO_2Se_2$

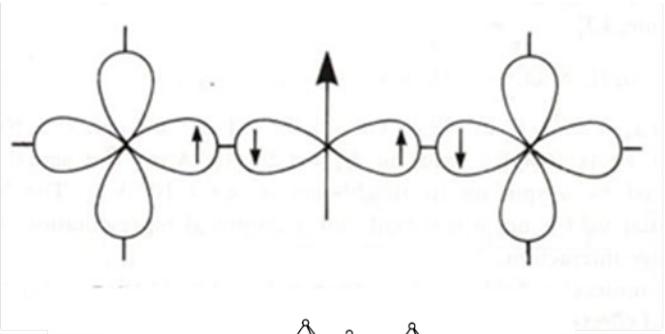

A_2MO_3Cl

n = 1 Ruddlesden-Popper Structure



	$A_2M^{4+}O_4$	$A_2M^{3+}O_3Cl$	$A_2M^{2+}O_2Cl_2$
A = Ca	Ti, Cr, Mn Ru Ir	Fe	Cu
A = Sr	Ti, Cr, Mn, Fe Mo, Tc, Ru, Rh Ir	Sc, V, Mn, Fe, Co, Ni	Co, Cu

ICSD



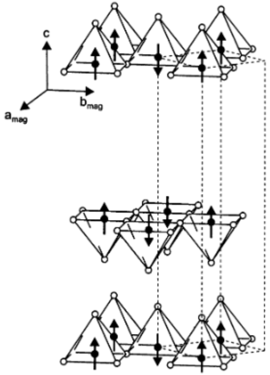
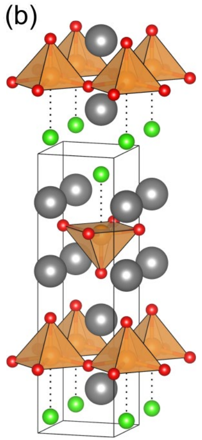


Figure 9. Magnetic cell of Sr_2MnO_3Cl showing the antiferromagnetically coupled Mn spins aligned along *z*. The nuclear cell is shown by the dotted lines.

Knee and Weller *Chem Mater* 2002

Coordination Requirements



	$A_2M^{3+}O_3Cl$
A = Ca	Fe
A = Sr	Sc, V, Mn Fe, Co, Ni

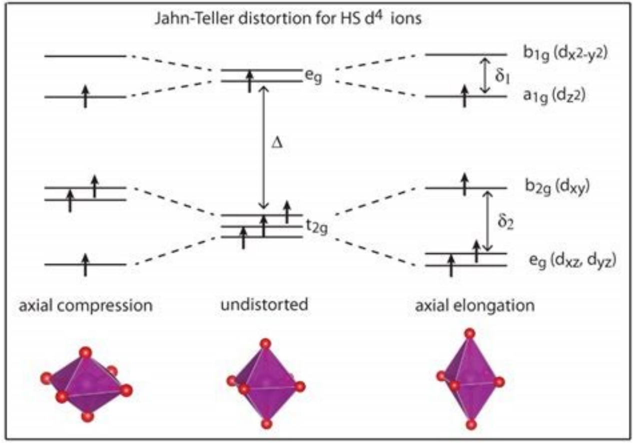
Tolerance Factor

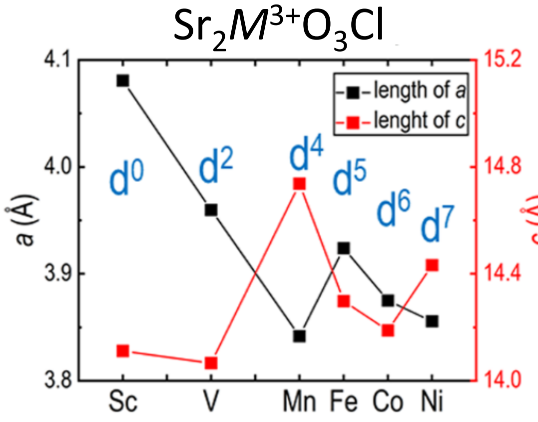
$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

Sr_2FeO_3Cl	0.92	c.f. *Pm*-3*m* $SrFeO_3$
Ca_2FeO_3Cl	0.88	*Pnma* $CaFeO_3$

Jahn-Teller Distortion

Mn^{3+} HS d^4





Kriworuschenko and Kahlenberg *Crystal Research and Technology*, 2002; Hector *et al. J Mater Chem* 2001, Sannes *et al. ACS Omega* 2023

Can we make Ca_2MnO_3Cl?

$2CaO + ½MnO_2 + ½MnCl_2$

Quartz tube sealed under vacuum

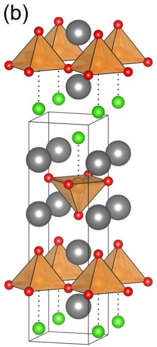
1×12h 850 °C

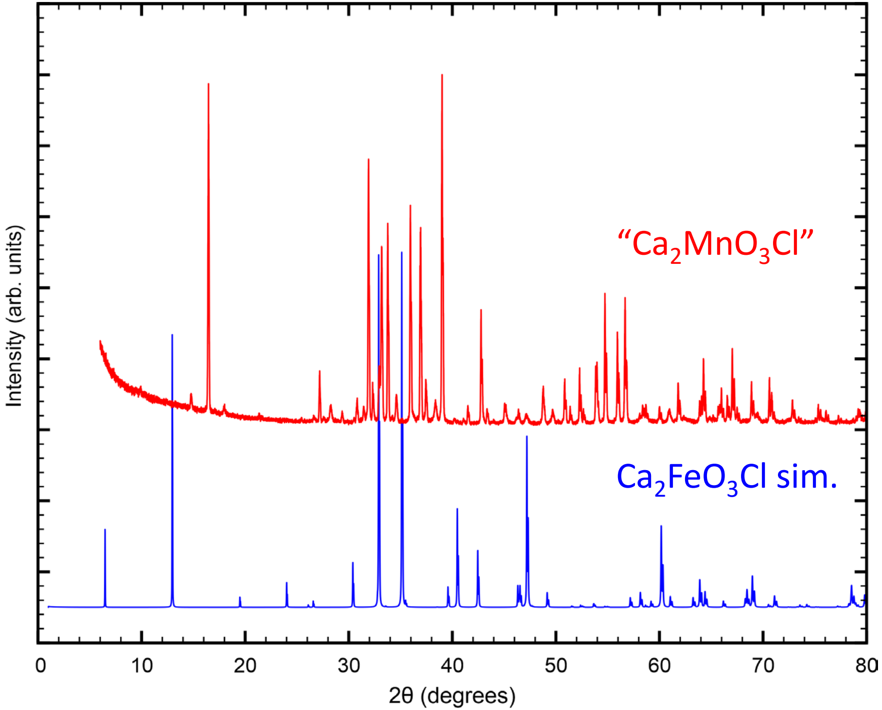
→ Orange powder
→ Moisture sensitive
(decomp. in days)

→ Sharp reflections
→ Not Ca_2FeO_3Cl structure

Structure solution

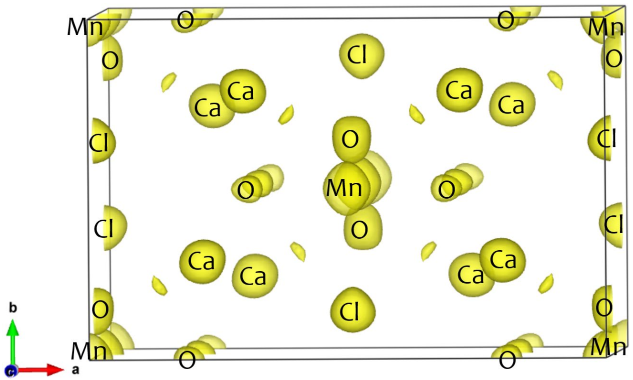
→ **TEM**

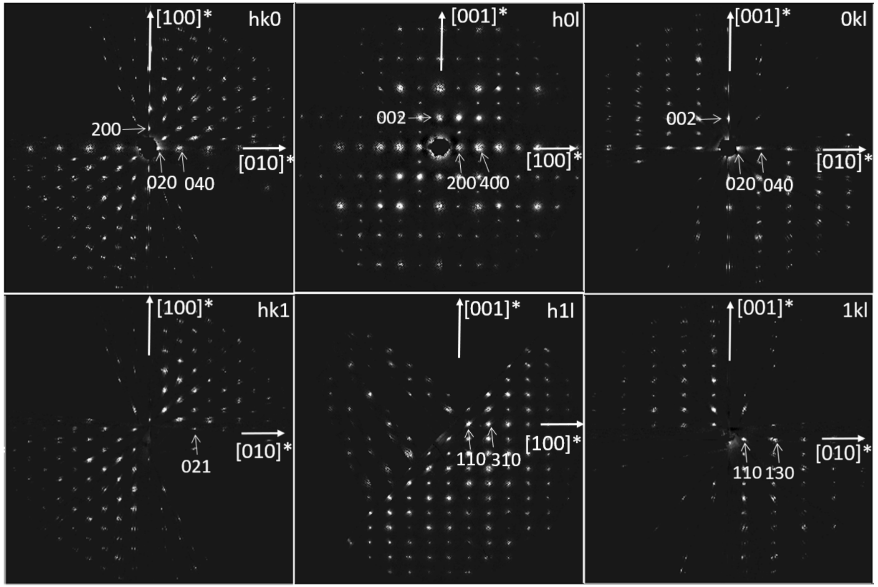




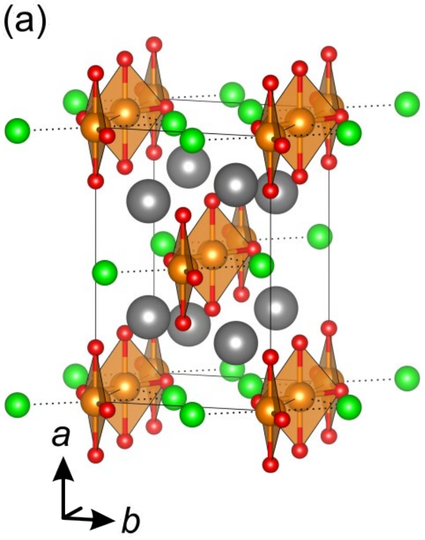
TEM

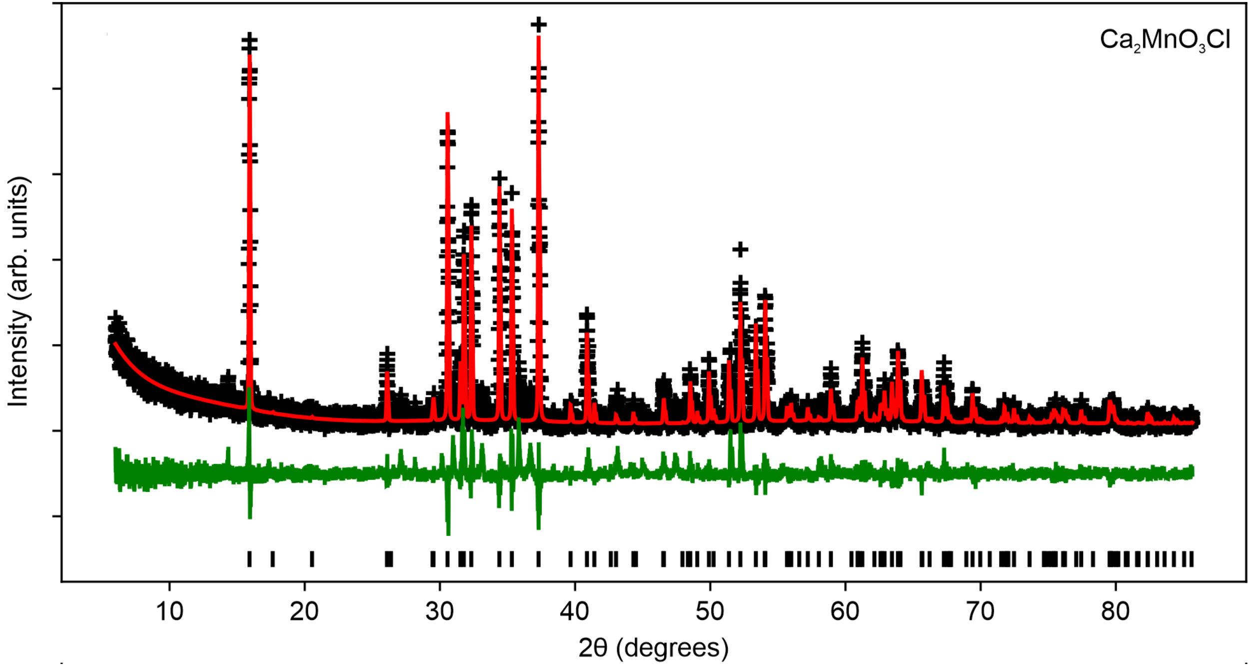
- EDX analysis (avg 10 crystallites):
  - $Ca_{2.0(1)}Mn_{1.3(1)}Cl_{0.7(1)}O_x$
- *Cmcm*
  - a = 9.75 Å
  - b = 6.49 Å
  - c = 6.58 Å
  - vol. = 416 Å^3





Refinement against Lab XRD

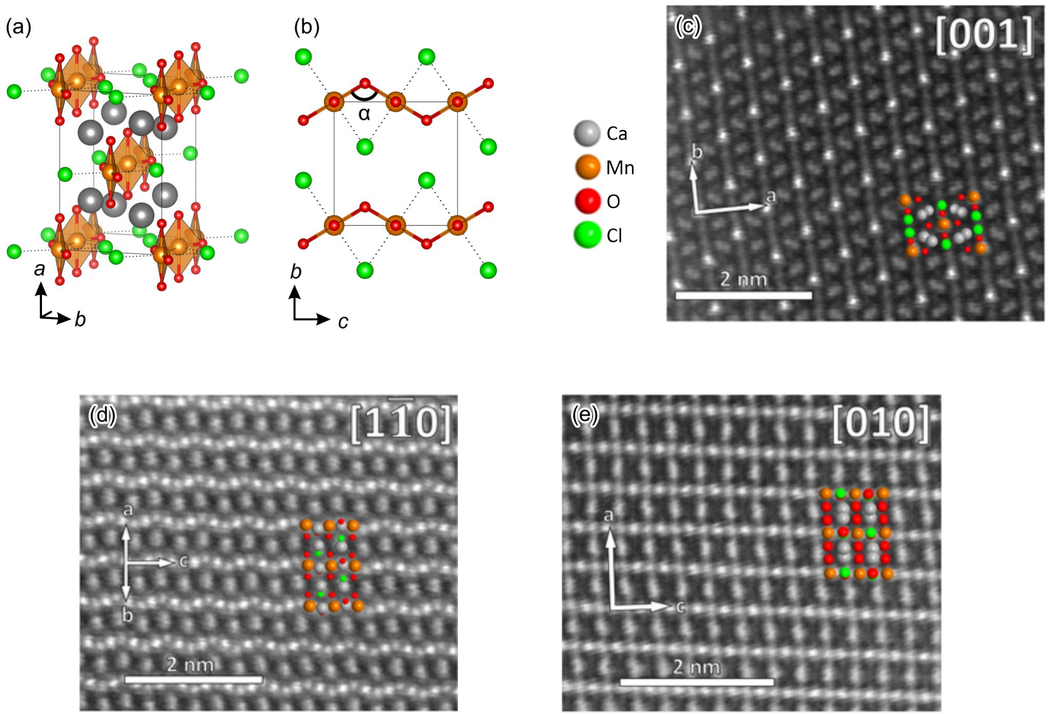




Crystal structure

- Chains of $Mn^{3+}O_4$ square-planes
- α ~ 120 °

Ca_2MnO_3Cl



	X = Cl
Mn-*X*	2.851(2) Å ×2
Mn-O1	1.909(3) Å ×2
Mn-O2	1.925(3) Å ×2
Mn BVS	**2.91**
Mn-Mn intrachain	3.288(2) Å
Mn-O1-Mn (α)	118.9(2) °
Mn-*X*-Mn	6.488 Å
Mn-Ca-Mn	5.855 Å

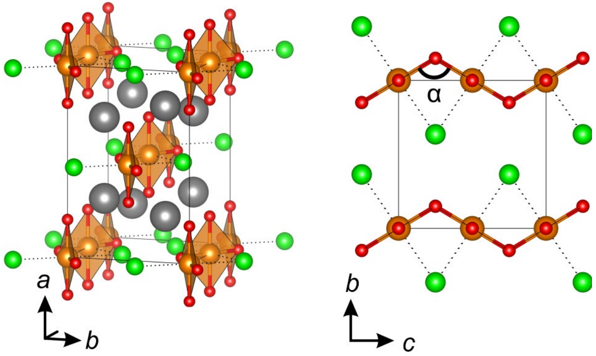
Ca_2MnO_3Br

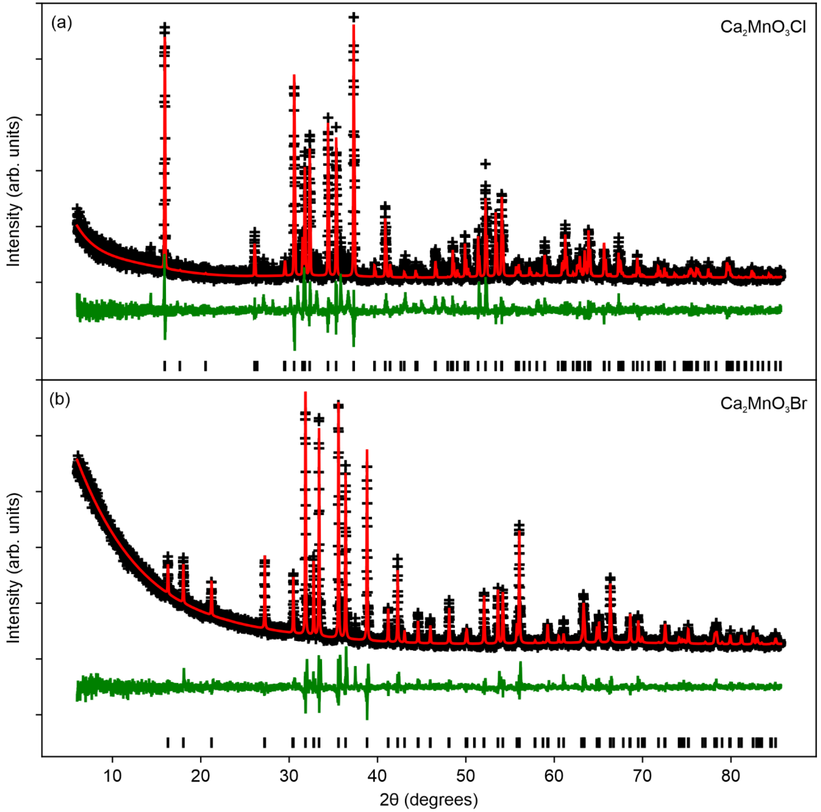
$2CaO + ½MnO_2 + ½MnBr_2$

Quartz tube sealed under vacuum

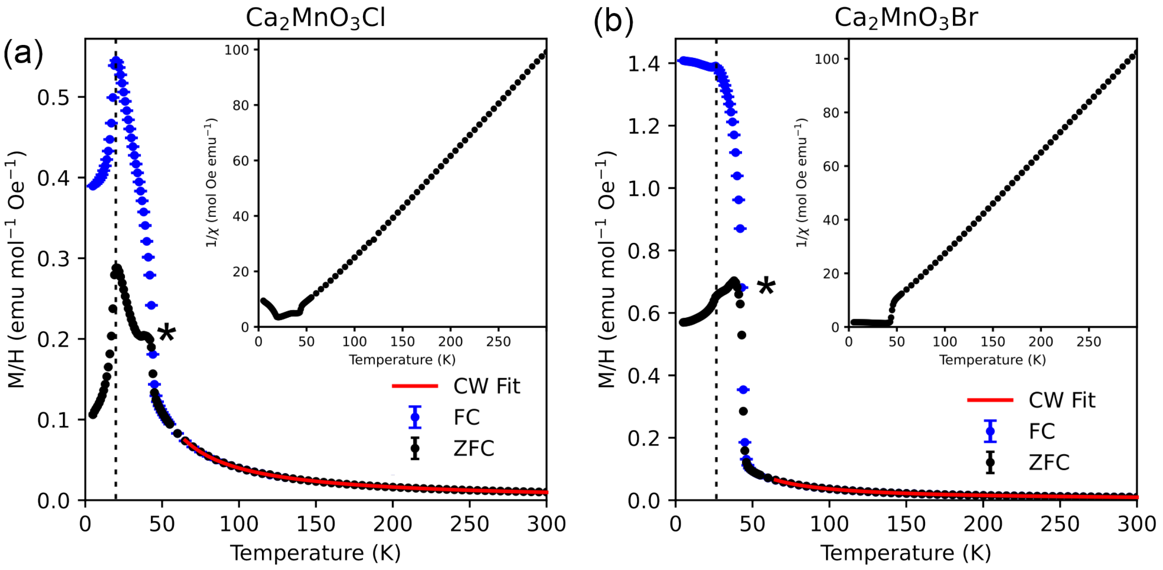
1×12h 850 °C

→ Orange powder
→ Moisture sensitive
(decomp. in hours)





Magnetic Properties



C = 3.23 emu K / mol and 3.04 emu K / mol

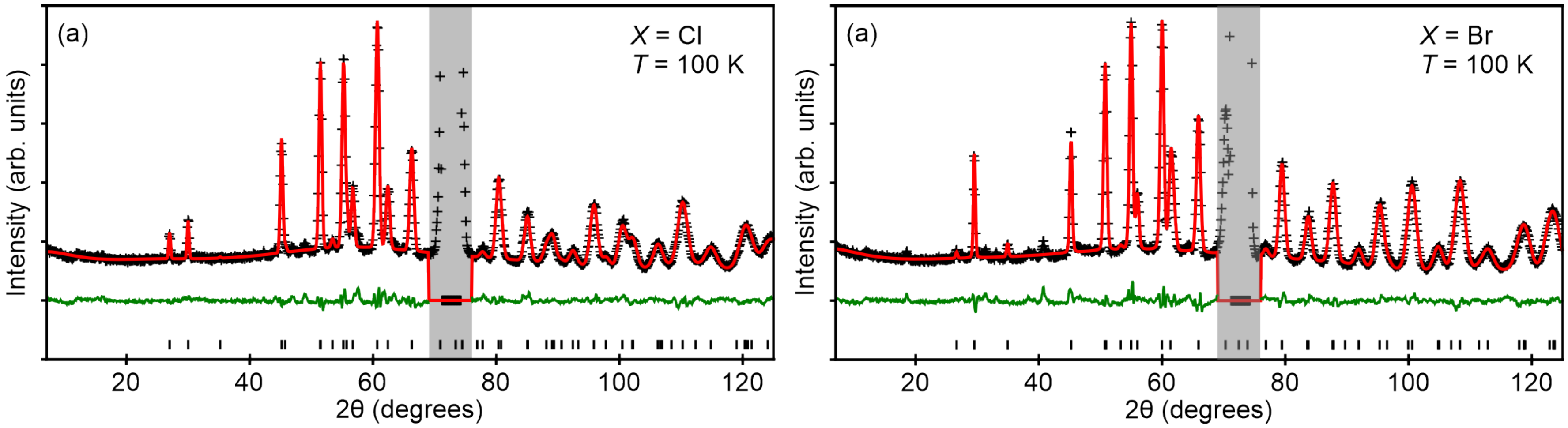
μ_{eff} = 5.09 μ_B and 4.93 μ_B vs. μ_{exp} = 4.90 μ_B

θ = 22 K and 19 K for X = Cl and Br respectively

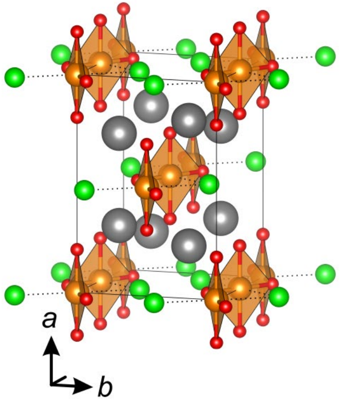
48 K (*) → FiM Mn_2O_3 impurity <1% by mass

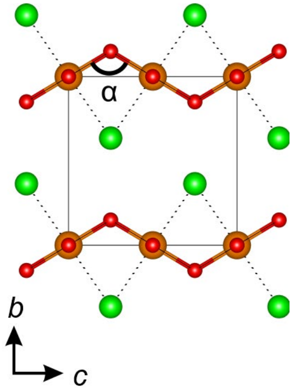
AFM T_N ~ 20 and 28 K (---)

D1b


(a)
X = Cl
T = 100 K
Intensity (arb. units)
20
40
60
80
100
120
2θ (degrees)
(a)
X = Br
T = 100 K
Intensity (arb. units)
20
40
60
80
100
120
2θ (degrees)

Structural Properties



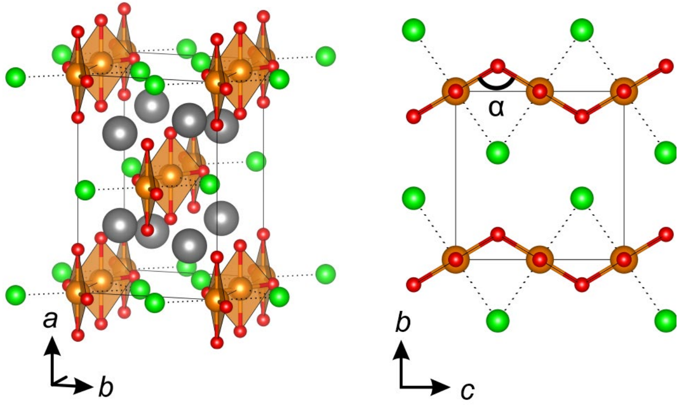


Ionic radii:

O^{2-}	1.40 Å
Cl^{-}	1.81 Å (+29%)
Br^{-}	1.96 Å (+40%)

	X = Cl	*X* = Br
Ca-*X*	3.122(4) Å ×1 2.945(3) Å ×1	3.125(3) Å ×1 3.027(3) Å ×1
Ca-O1	2.250(4) Å ×1	2.253(4) Å ×1
Ca-O2	2.468(2) Å ×2 2.337(3) Å ×2	2.479(3) Å ×2 2.353(3) Å ×2
Ca BVS	**2.06**	**1.63**
Mn-*X*	2.851(2) Å ×2	2.898(3) Å ×2
Mn-O1	1.909(3) Å ×2	1.915(2) Å ×2
Mn-O2	1.925(3) Å ×2	1.932(3) Å ×2
Mn BVS	**2.91**	**2.57**
Mn-Mn intrachain	3.288(2) Å	3.285(2) Å
Mn-O1-Mn (α)	118.9(2) °	118.2(2) °
Mn-*X*-Mn	6.488 Å	6.536 Å
Mn-Ca-Mn	5.855 Å	5.936 Å

Structural Properties



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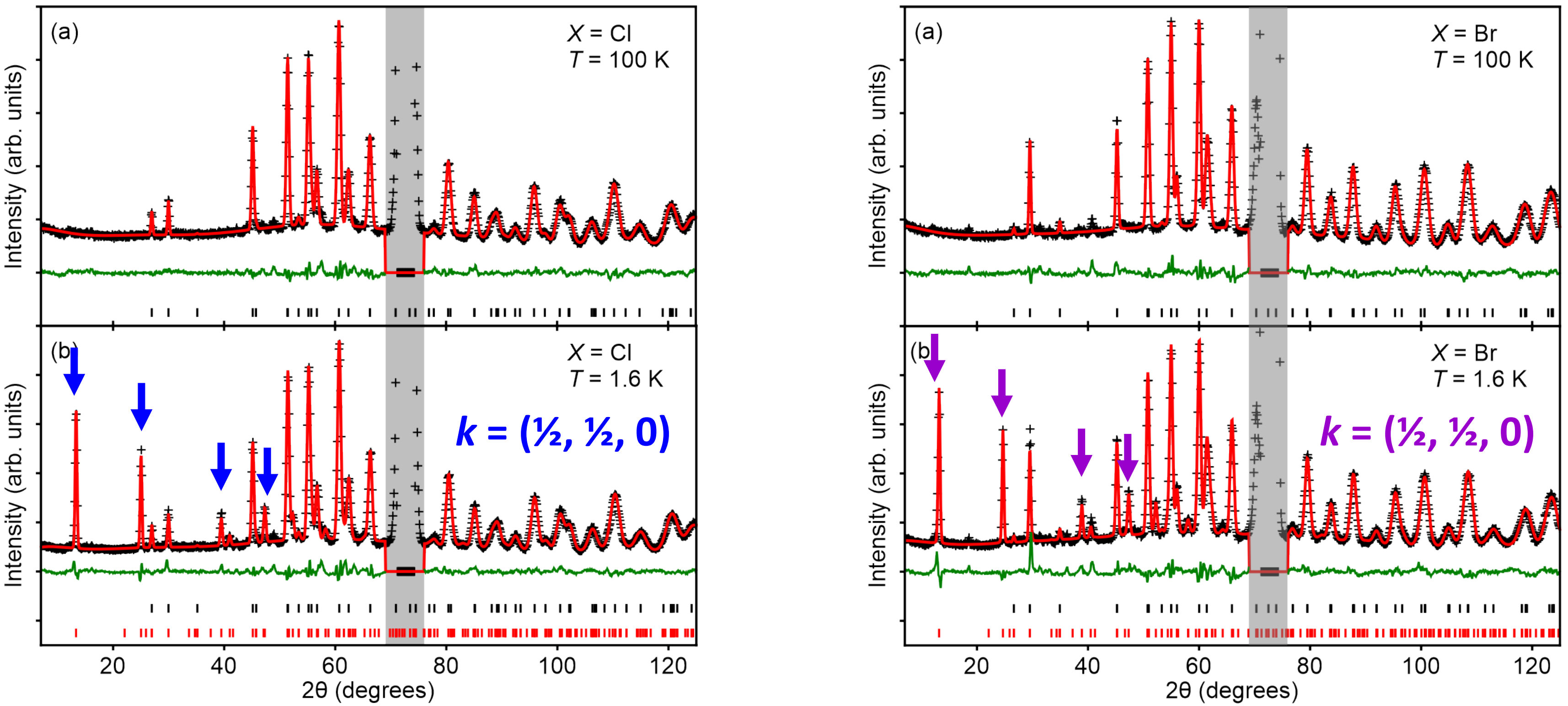
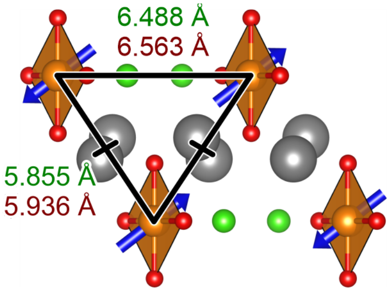
Mn-O1-Mn (α)	118.9(2) °	118.2(2) °
Mn-*X*-Mn	6.488 Å	6.536 Å
Mn-Ca-Mn	5.855 Å	5.936 Å

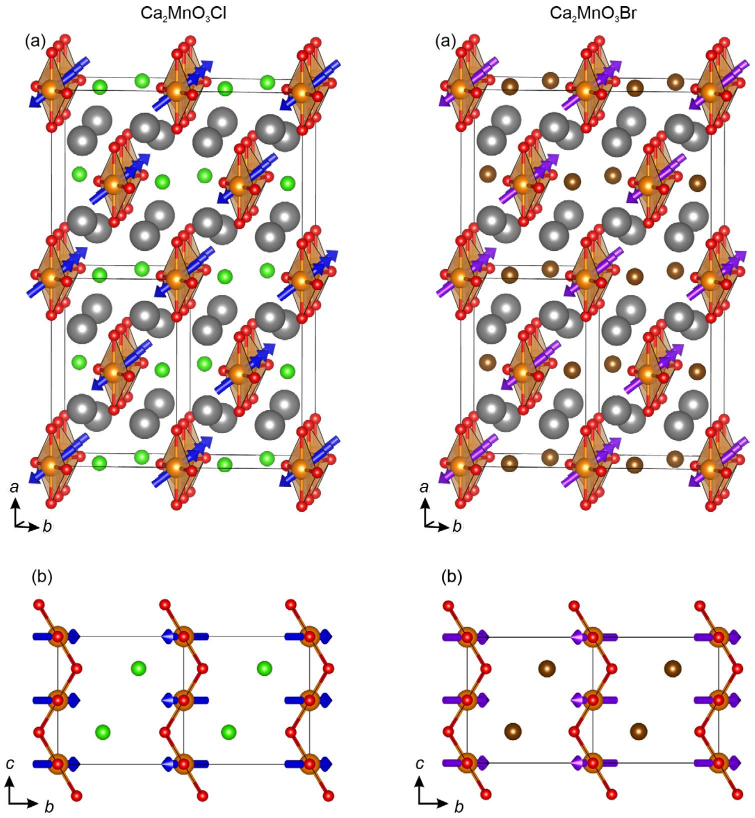
Magnetic Properties / D1b



Magnetic structure

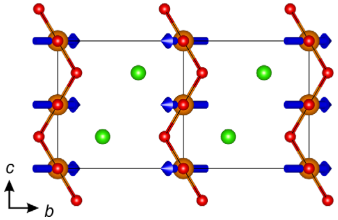
- FM chains coupled AFM
- Refined 3.7(1) and 3.5(1) μ_B
- Interaction through halide responsible for long range order





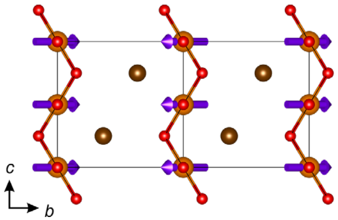
Halide interactions

Ca_2MnO_3Cl

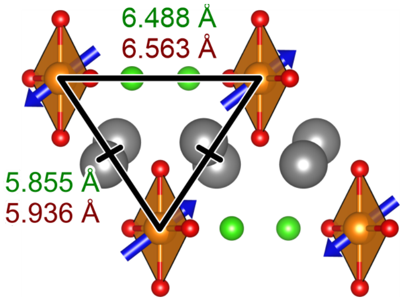


T_N = 20 K
H_c = 2.0 T

Ca_2MnO_3Br



T_N = 28 K
H_C = 4.8 T



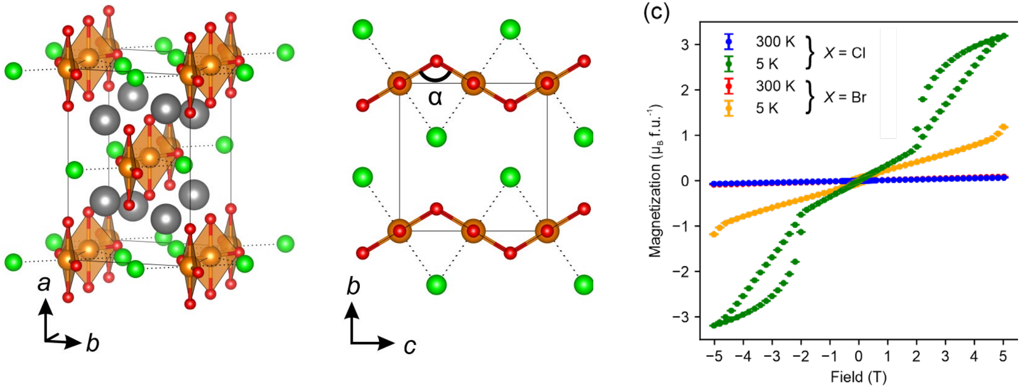
Mn-…Cl…-Mn < Mn-…Br…-Mn

T_N	X = Cl	X = Br
Ca_2MnO_3X	**20 K**	**28 K**
MnX_2	1.96 K	2.16 K
$MnX_2·4H_2O$	1.62 K	2.12 K
$[(CH_3)_3NH]MnX_3·4H_2O$	0.98 K	1.58 K

McGuire, *et al. Crystals* 2017; Westphal, *et al. J. Phys. C: Solid State Phys.* 1980; Westphal, *et al. J. Phys. C: Solid State Phys.* 1982; *Extended Interactions between Metal Ions: In Transition Metal Complexes* 1974; *Magnetochemistry* 1986

Conclusion

- Synthesis of two oxyhalides w/ novel structure type
- 1-dimensional chains of square-planar $S = 2$ Mn^{3+}
- FM chains coupled AFM
- Determinant magnetic interaction through halide
- Spin-flop transitions at low T



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Thank you for you attention