Supporting Information

Anisotropic Triangular Lattice Realized in Rhenium Oxychlorides $A_3ReO_5Cl_2$ (A = Ba and Sr)

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There is a subtle difference between the crystal structures of BROC and SROC originated from the size of A-site cations. The anisotropic displacement parameters (ADPs, U_{ij}) for Cl sites refined based on the structure of $Ba_3WO_5Cl_2$ converged to reasonable values of 0.01–0.077 Å^2 for BROC (Table S3), while, for SROC, they became anomalously large: U_{33}(Cl1) = 0.33(3) Å^2, U_{11}(Cl2) = 0.54(5) Å^2, which implies a tendency for the Cl1 and Cl2 sites to split along the *c* and *a* directions, respectively. A more reasonable fitting for SROC was obtained by assuming Cl site splittings: the Cl1 site at 4*c* was split into two 8*f* sites with half occupancy along the *c* direction, and the Cl2 site at 4*b* was split into two 8*e* sites with half occupancy along the *a* direction (Fig. S1 and Table S2). As a result, the reliability of refinement was improved from R_{wp} = 4.66% to 2.48%. The structure is stable for large Ba ions but not so for small Sr ions, which may be compensated by the site splittings of Cl sites.

Although the ADPs for BROC and SROC become reasonably small by taking into account the splittings of the Cl, some of them are non-spherical, implying that there is a further structural instability in this structure. The ADPs of O2, Cl1 and Cl2 are stretched perpendicular to the *b, a*, and *c* axes, respectively, probably because the bond between Sr/Ba2 and these sites are weak and unstable. It is speculated that the size mismatch between Cl layers and A_3ReO_5 layers are responsible for this structural instability inducing the anisotropic and large ADPs.

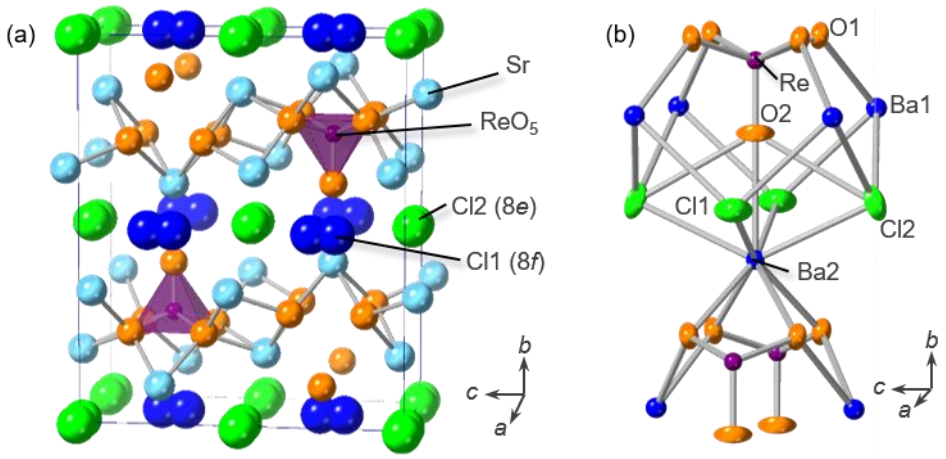

Figure S1. (a) Crystal structure of Sr_3ReO_5Cl showing the site splitting of Cl1 and Cl2 at the 8*f* and 8*e* sites along the *c* and *a* axes, respectively. (b) The anisotropic displacement parameters (ADPs) for BROC are shown by the ellipsoids. The ADPs of O2, Cl1, and Cl2 are stretched perpendicular to the bonds between Ba2 and these sites.

Table S1. Crystal data and structure refinement for $Ba_3ReO_5Cl_2$ and $Sr_3ReO_5Cl_2$.

Empirical formula	$Ba_3ReO_5Cl_2$	$Sr_3ReO_5Cl_2$
Formula weight (g mol^{-1})	749.12	599.96
Temperature (K)	296(2)	296(2)
Wavelength	Mo$K\alpha$ (λ = 0.71075 Å)	Mo$K\alpha$ (λ = 0.71075 Å)
Absorption coefficient (mm^{-1})	26.196	34.401
F(000)	1269	1052
θ range for data collection (deg)	3.42 to 27.45	3.09 to 27.49
Index ranges	$-7 \le h \le 7$, $-18 \le k \le 18$, $-14 \le l \le 14$	$-7 \le h \le 7$, $-16 \le k \le 16$, $-14 \le l \le 14$
Reflections collected	4407	3978

Table S2. Structural parameters for $Ba_3ReO_5Cl_2$ and $Sr_3ReO_5Cl_2$.

Atom	Wyckoff positions	Symmetry	x	y	z	occupancy	$100U_{eq}$ (Å^2)
$Ba_3ReO_5Cl_2$, space group *Cmcm* (No. 63), a = 5.79424(18) Å, b = 13.9508(4) Å, c = 11.4414(5) Å, Z = 4, V = 924.86(5) Å^3, R_{wp} = 2.35%, R_p = 5.67%							
Ba1	8*f*	*m*..	0	0.34818(3)	0.54316(4)	1	1.472(16)
Ba2	4*c*	*m*2*m*	0.5	0.40260(5)	0.25	1	1.090(17)
Re	4*c*	*m*2*m*	0	0.23867(3)	0.25	1	0.993(14)
O1	16*h*	1	0.2222(7)	0.2779(3)	0.3629(3)	1	1.48(8)
O2	4*c*	*m*2*m*	0	0.1161(7)	0.25	1	3.6(3)
Cl1	4*c*	*m*2*m*	0	0.4939(2)	0.25	1	2.66(7)
Cl2	4*b*	2/*m*..	0.5	0.5	0.5	1	4.28(10)
$Sr_3ReO_5Cl_2$, space group *Cmcm* (No. 63), a = 5.6492(3) Å, b = 13.1886(6) Å, c = 11.1144(5) Å, Z = 4, V = 828.09(7) Å^3, R_{wp} = 2.48%, R_p = 5.59%							
Sr1	8*f*	*m*..	0	0.34264(5)	0.53964(6)	1	1.569(19)
Sr2	4*c*	*m*2*m*	0.5	0.40018(7)	0.25	1	1.03(2)
Re	4*c*	*m*2*m*	0	0.23691(3)	0.25	1	0.908(15)
O1	16*h*	1	0.2281(6)	0.2797(3)	0.3655(3)	1	1.39(7)
O2	4*c*	*m*2*m*	0	0.1073(6)	0.25	1	3.0(2)
Cl1	8*f*	*m*..	0	0.4984(3)	0.2880(3)	0.5	2.39(9)
Cl2	8*e*	2..	0.5940(8)	0.5	0.5	0.5	2.79(9)

Table S3. Anisotropic displacement parameters U_{ij} (Å^2) for $Ba_3ReO_5Cl_2$ and $Sr_3ReO_5Cl_2$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$Ba_3ReO_5Cl_2$						
Re1	0.0096(2)	0.0101(2)	0.0100(2)	0	0	0
Ba1	0.0185(3)	0.0125(2)	0.0131(3)	-0.00006(16)	0	0
Ba2	0.0103(3)	0.0122(3)	0.0103(3)	0	0	0
Cl1	0.0154(13)	0.0178(14)	0.0464(19)	0	0	0
Cl2	0.077(3)	0.038(2)	0.0139(15)	-0.0100(13)	0	0
O1	0.0107(19)	0.022(2)	0.0113(17)	0.0021(15)	0.0014(15)	-0.0007(16)
O2	0.053(7)	0.009(4)	0.045(6)	0	0	0
$Sr_3ReO_5Cl_2$						
Re1	0.0046(2)	0.0099(2)	0.0128(2)	0	0	0
Sr1	0.0139(4)	0.0154(4)	0.0178(4)	0.0037(3)	0	0
Sr2	0.0070(4)	0.0110(4)	0.0130(5)	0	0	0
Cl1	0.0138(16)	0.0179(16)	0.040(3)	-0.0099(16)	0	0
Cl2	0.036(2)	0.027(2)	0.0206(18)	-0.0055(16)	0	0
O1	0.0071(17)	0.0207(18)	0.0138(17)	0.0025(15)	-0.0009(15)	-0.0008(14)
O2	0.027(5)	0.005(3)	0.057(6)	0	0	0

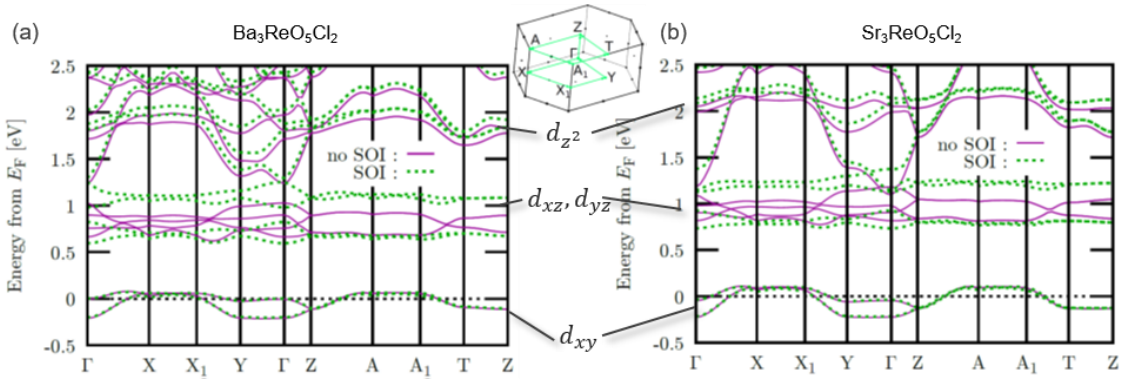

Figure S2. Band structures of (a) BROC and (b) SROC. The Brillouin zone and *k*-path and the orbital characters of the bands are shown between them. The magenta solid and green dashed lines represent the energy bands calculated with and without SOIs, respectively. The occupied d_{xy} orbitals, which are responsible for the magnetism, are not influenced by SOIs, while the degenerated d_{zx} and d_{yz} bands are strongly affected.