Supplementary information

Layered anion ordering in oxide chloride Ca_2TlO_3Cl

Lars Botolv Ekeli Bråtalien,[a] Ola Nilsen, [a] Dipankar Saha, [a] Chris Mohn, [a] Athanasios Chatzitakis, [b] and Martin Valldor [a]*

[a] *Department of Chemistry, Centre for Materials Science and Nanotechnology, University of Oslo, Sem Sælands vei 26, NO-0371 Oslo, Norway*
[b] *Department of Chemistry, Centre for Materials Science and Nanotechnology, University of Oslo, Gaustadalléen 21, NO-0349 Oslo, Norway*

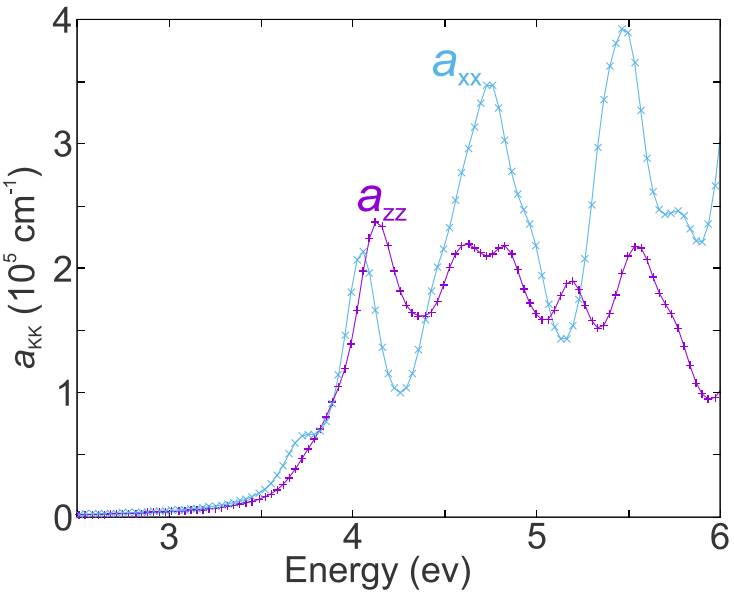
S1. HSE06 optimized (relaxed) structural parameter of Ca_2TlO_3Cl.
crystal system Hexagonal, space group $P6_3/mmc$ (No. 194)
a = 3.890 Å, c = 18.710 Å

Site	Wyck.	x	y	z
Tl1	2*c*	2/3	1/3	3/4
Ca1	4*f*	1/3	2/3	0.6087
Cl1	2*a*	0	0	1/2
O1	4*f*	2/3	1/3	0.6361
O2	2*d*	1/3	2/3	3/4

S2. The calculated band gaps together with the location of the critical points for the different DFT calculation methods.

Theory	E_g	CBM	VBM
PBE	1.656 (indirect)	0.000 0.000 0.000	0.3333 0.3333 0.0000
MBJ	2.64 (indirect)	0.000 0.000 0.000	0.3333 0.3333 0.0000
HSE06	2.741 (indirect)	0.000 0.000 0.000	0.3333 0.3333 0.0000
G_0W_0	2.840 (indirect)	0.000 0.000 0.000	0.3333 0.3333 0.0000

S3. Calculated absorption coefficients a_{xx} (a_{zz}), representing the crystallographic a-axis (c-axis)



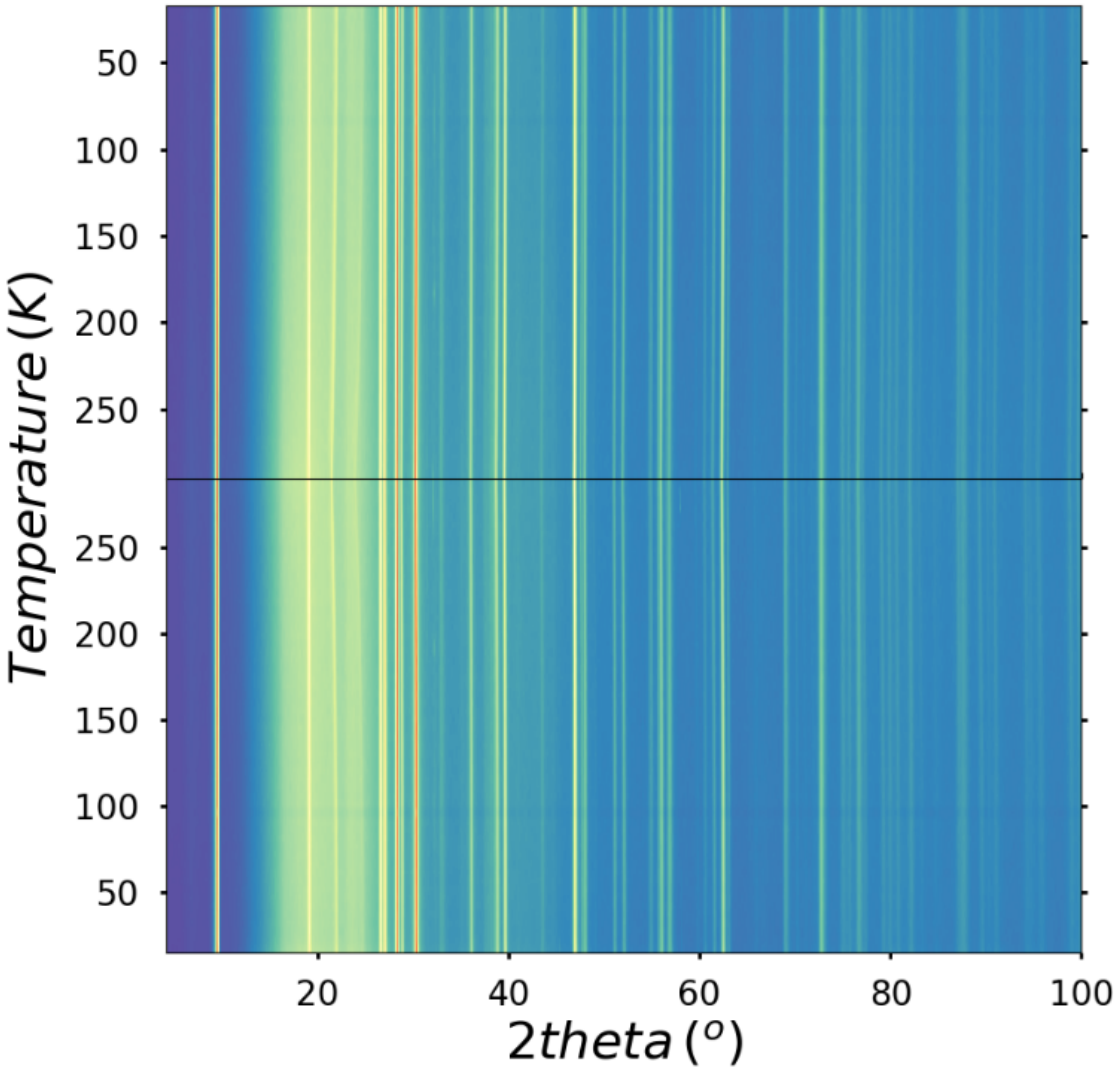
S4. From Rietveld refinement of **Sample 2**, the follow parameters were obtained:

R_p	0.083
R_{wp}	0.109
R_{exp}	0.060
CHI^2	1.65
Space group	$P6_3/mmc$
a (Å)	3.87968(5)
c (Å)	18.64191(4)
V (Å^3)	243.004(8)
Density (g cm^{-3})	5.029

Atomic coordinates and thermal parameters after the Rietveld refinement.

Site	Wyck.	x	y	z	Atom	Occ.	$B_{eq.}$
Tl1	2c	2/3	1/3	3/4	Tl	1	2.94(2)
Ca1	4f	1/3	2/3	0.608(2)	Ca	1	2.80(1)
Cl1	2a	0	0	1/2	Cl	1	2.22(1)
O1	4f	2/3	1/3	0.631(4)	O	1	2.36(2)
O2	2d	1/3	2/3	3/4	O	1	2.34(4)

S5. Temperature dependent powder x-ray diffraction data from a Huber camera.



S6. The reflectance spectroscopic raw data.