University of Dundee

Improper Ferroelectrics and Domain Wall: Structure, Properties and Negative Capacitance

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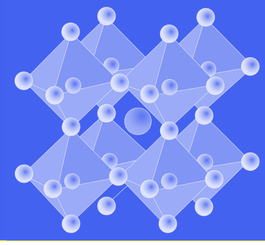
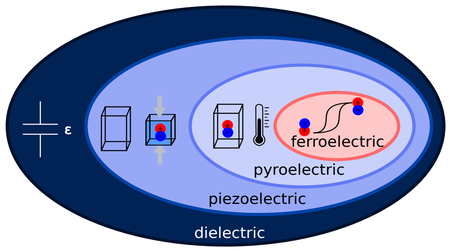
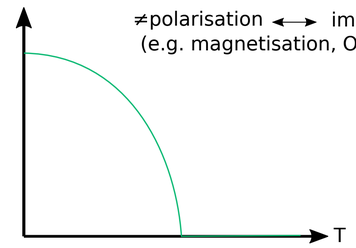


Ferroelectrics: proper and improper



order parameter =polarisation ⟷ proper

≠polarisation ⟷ improper
(e.g. magnetisation, O-tilts)



Boracite $M_3B_7O_{13}X$

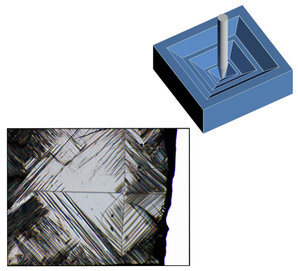
First magnetoelectric discovered

Strong pyroelectric

Improper ferroelectric

soft mode: X_5 phonon mode [1]
⟶ Γ_4 slave mode (P_S)

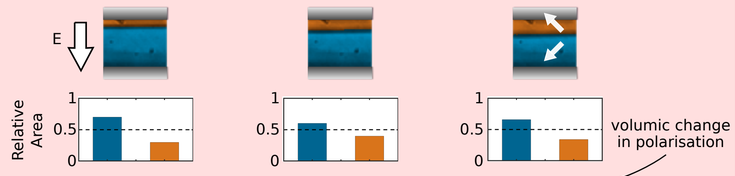
Cu-Cl Boracite $Cu_3B_7O_{13}Cl$



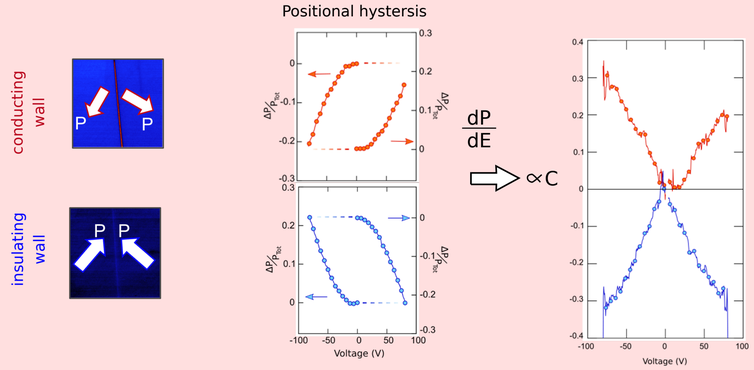
Pressure induced charged walls
(few mm) [2]

Anomalous motion

Charged walls move under the application of an electric field



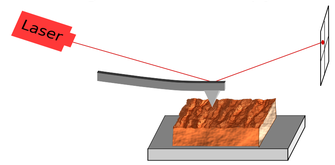
Positional hystersis



Negative capacitance

Nanoscale characterisation

Scanning Probe Microscopy



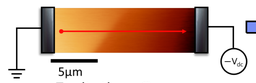
Negative capacitance

Charge Gradient Microscopy (CGM)

ΔQ at wall

Excitation: ∅
Dectection: I_{DC} tip

Kelvin Probe Force Microscopy (KPFM)

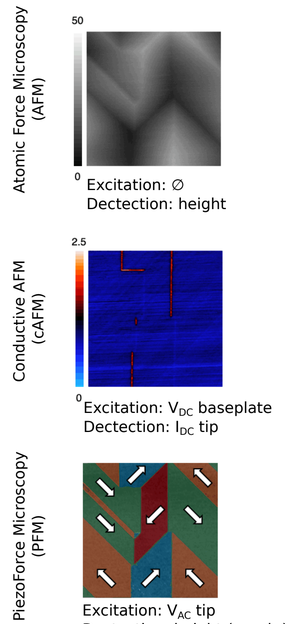


No inversion of electric field

Excitation: ∅
Dectection: V_{DC} tip

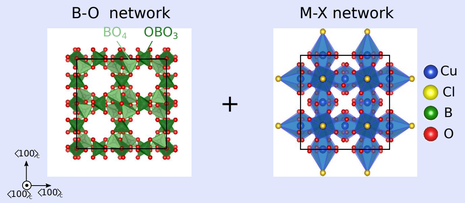
Local negative capacitance

Domain orientation and charges at interfaces

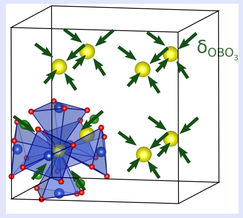


Structure

Superposition of two sublattices

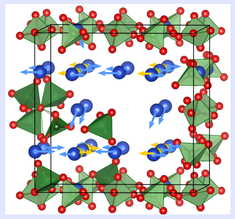


High-temperature: piezoelectricity
$F\bar{4}3m$



M-X bipyramid ($a^-a^-a^-$ 41°)

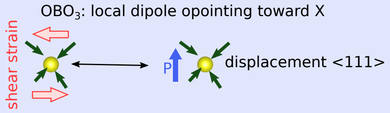
Low-temperature: ferroelectricity
$P2c2_1$



M-X antiparallel displacement in (001) X_5 mode
+ canted from [001] Γ_4 mode

Bond breaking: 1 OBO_3 ⟷ BO_3

OBO_3: local dipole opointing toward X

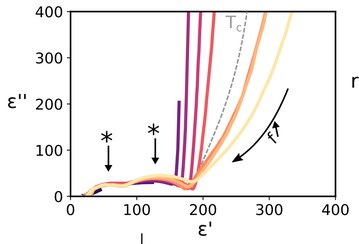


Piezoelectricity ⟷ B-O network

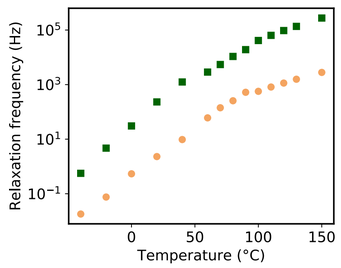
Ferroelecricity ⟷ M-X network

Electrical properties

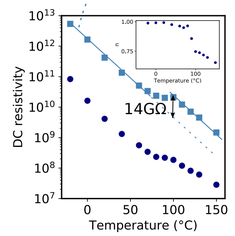
Dielectric dispersion: 1mHz-1MHz



2 relaxations



resistivity vs T



slope: semiconductor or defect activated?

Change in resistivity at T_c

disappearance of charged walls?

Vogel-Fulcher

	T_f(K)	E_a(eV)
relaxation 1	-5±9	0.63±0.04
relaxation 2	-12±11	0.62±0.05

Defect activated relaxations

Defects driven electrical properties

Summary

Boracite is a versatile class of materials due to the flexibility of its structure: different functional properties can be "incorporated" on each sublattice.
wit its charged domain walls that can be injected and controlled, Cu-Cl boracite is a particularly interesting member of this family.
Although, macroscopically Cu-Cl boracite behaves as a positive capacitance (with some influence of defects), focusing on one domain walls demonstrate the opposite: **negative capacitance**.
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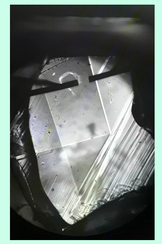
The physical origin of the negative capacitance still remains elusive, but it is hpothesised that it has to do with long-range reorganisation of domains and an overall decrease in elastic energy



References

[1] Feng, J.S. *et al.* "Designing Switchable Near Room-Temperature Multiferrois via the Discovery of a Novel Magnetoelectric Coupling." New J. Phys. **20**, 053025 (2018)

[2] McQuaid, R.G.P., et al. "Injection and Controlled Motion of Conducting Domain Walls in Improper Cu-Cl Boracite" Nat. Commun. **8**, 15105 (2017)

[3] Guy, J.G.M, CC *et al.* "Anomalous Mortion of Charged Domain Walls and Associated Negative Capacitance in Copper-Chlorine Boracite." Adv. Mater. (2021) doi: 10.1002/adma.202008068

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