Influence of charged walls and defects on DC resistivity and dielectric relaxations in Cu-Cl boracite.

Supplementary Material

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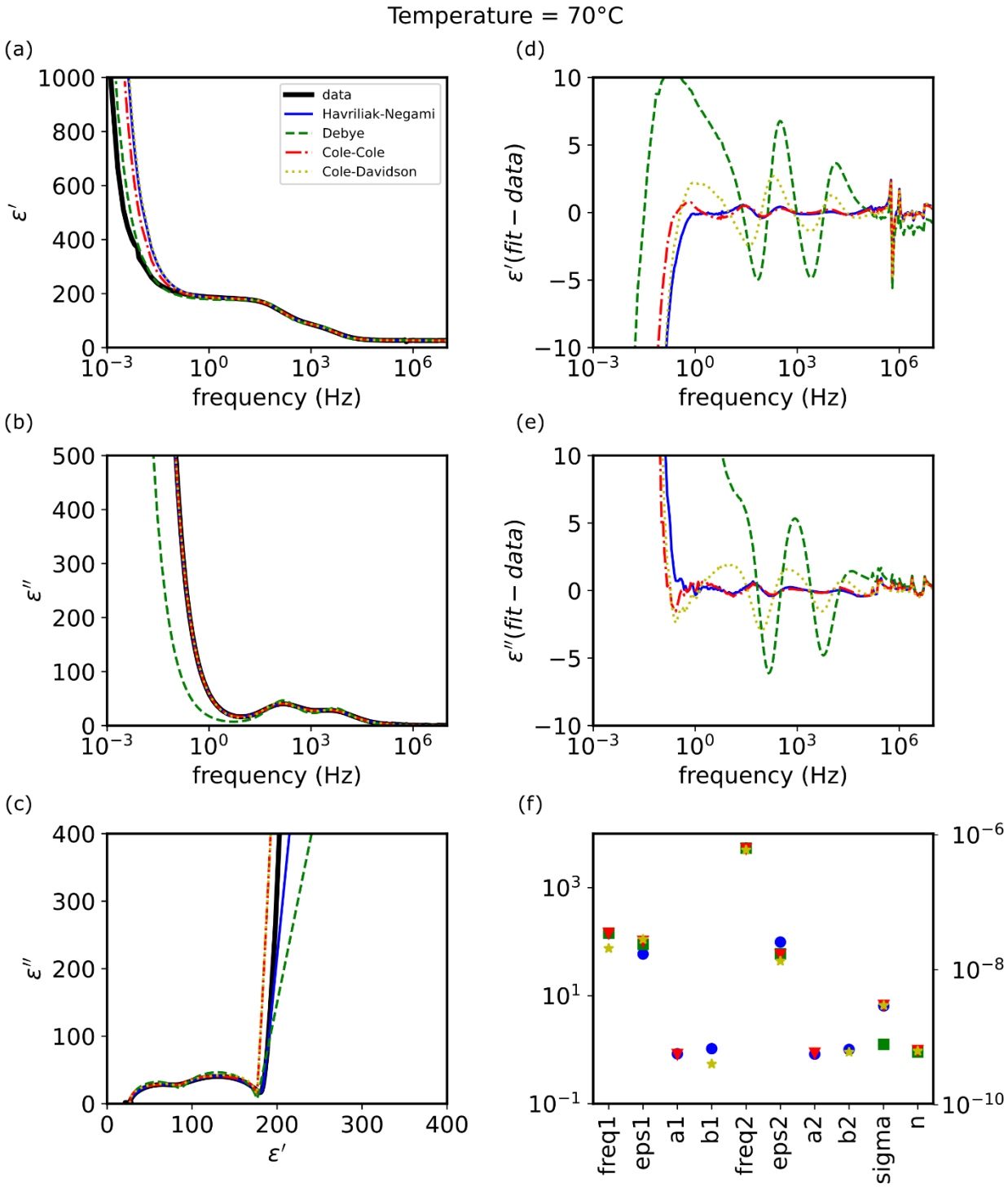


Supplementary Figure S1 Comparison of the quality of the fit from Debye, Cole-Cole, Cole-Davidson and Havriliak-Negami function models. (a-c) present the fit and the data together, (d-e) present the residuals and (f) presents the value obtained from the different fit.

Havriliak-Negami fitting function $\varepsilon^* = \frac{\Delta\varepsilon}{\left[1+i\left(f/f_{r,1}\right)^a\right]^b} + \frac{\Delta\varepsilon}{\left[1+i\left(f/f_{r,2}\right)^a\right]^b} + \frac{\sigma}{\varepsilon_0(i2\pi f)^n}$

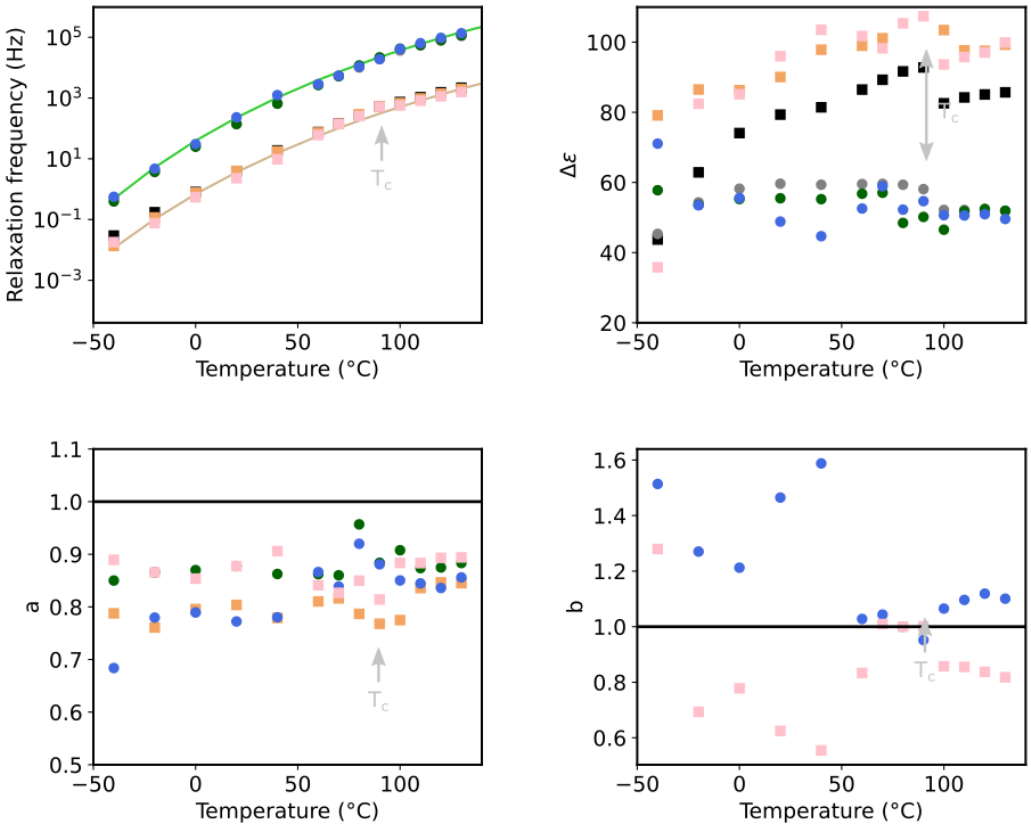
The difference between HN and the other models is in the exponents a and b, which describe the broadening and asymmetry of the relaxation peak, respectively. Under the assumptions of a Cole-Cole relaxation, b=1, Cole-Davidson a=1 and Debye relaxation a=b=1.

The fits obtained at 70°C are presented (a-c). In thick black line, the experimental data, in thin blue line, the fit obtained with the HN mode, in dashed green line, the fit obtained with the Debye model, in red dash-dot line, the Cole-Cole model and in yellow dotted line, the Cole-Davidson model.

The difference between the fit and the data are presented (d,e). The colour code remains the same as for (a-c).

The values of all the fitting parameters obtained with the different models at 70°C are presented in (f). The values of conductivity σ is presented on the right axis (because of the difference in magnitude compared with the rest of the values).

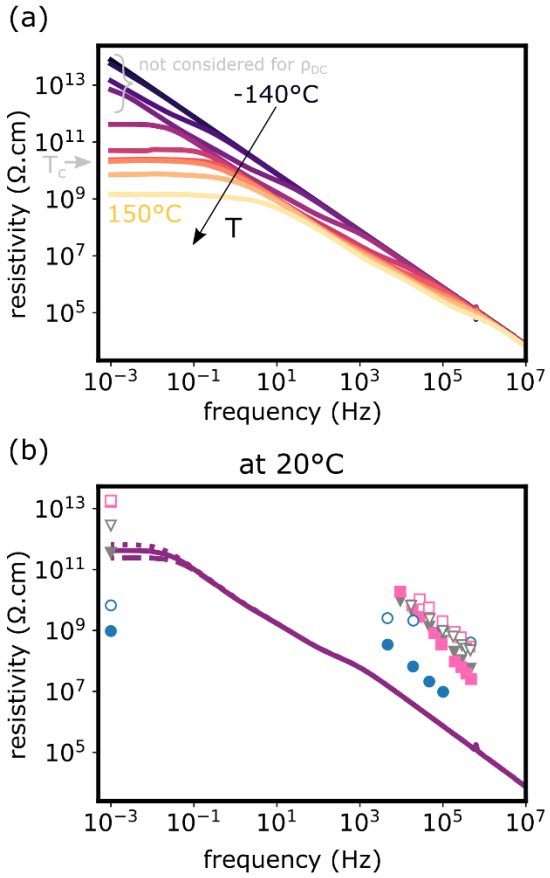
The difference between the two fits is noticeable at low frequencies, when describing the resistive component. We can, however, notice that the relaxations are reasonably modelled, with the Debye model despite a reduced quality in the description of the shape of the relaxations. The Cole-Cole model seems the better choice here with a reasonable number of fitting parameters and a good description of the complex dielectric spectrum.



Supplementary Figure S2 Comparison fitting results Havriliak-Negami (HN), Cole-Cole and Debye models on the relaxations.

The relaxation frequencies, amplitudes and the two exponents a and b are presented in this figure. In squares, the high frequency relaxation and in circles, the low frequency one. Green and yellow correspond to the Cole-Cole fit , pink and blue represents HN and black and grey, Debye model.

The difference between the three fits is quite small besides from the a and b exponent. We can notice also a small reduction in the noise of the relaxation amplitudes, when reducing the number of exponents used (HN quite noisy, Cole-Cole less, Debye the least).

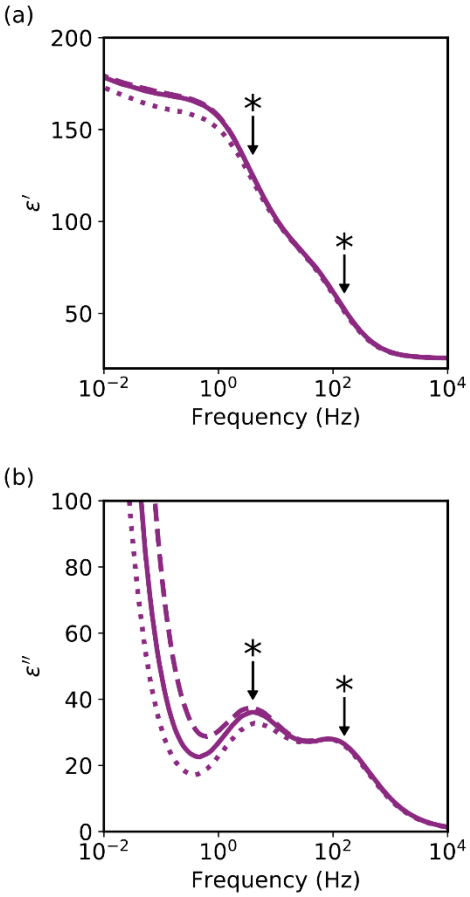


Supplementary Figure S3: Frequency dispersion of resistivity

(a) For different temperatures. It can be seen that at high temperature the resistivity plateaus at low frequencies indicating that the value is the DC value.

Data below T = -50°C were not considered for evaluation of the DC resistivity, since a low-frequency plateau was not observed at lower T.

(b) At 20°C, for different samples and thermal history. The lines represent our measurements on the same sample after different thermal treatment: before any cooling cycle (dashed line), after cooling at -140°C (full line) and after heating at 150°C (dotted line) Symbols represent measurements reported by Schmid and Peterman[1] different samples and domain configurations (open symbols correspond to single domain measurements)



Supplementary Figure S4 Influence of run cycle on the dielectric relaxations

The (a) real and (b) imaginary part of the permittivity are presented before any cooling cycle (dashed line), after cooling at -140°C (full line) and after heating at 150°C (dotted line)

Supplementary Note 1

As a first step in the analysis and with no a prirori regarding the physics associated with the change in resistivity with temperature, two temperature dependences were considered: (i) increase in the number of charged carriers, due to the temperature dependence of the Fermi-Dirac function and (ii) activated hopping between potential wells described as follows

$$(i) \quad \rho_{DC} = \rho_0 e^{-\alpha T} \quad and \ (ii) \quad \rho_{DC} = \rho_0 e^{\frac{E_a}{k_B T}}$$

where ρ_0 is a prefactor representing either the resistivity at T=0 K (i) or at infinite temperature (ii), α is a growth constant, E_a the activation energy and k_B the Boltzmann constant.

The description based on activated temperature dependence is more commonly used for dielectrics than that assuming intrinsic semiconductor behaviour, since defects are often the source of the DC conductivity. In the present case, the change in conductivity observed at charged walls could lead to an increase in the free charge carrier density with increasing temperature, hence suggesting a more intrinsic semiconductor behaviour[2–4]. This is particularly pertinent since the disappearance of domains at the phase transitions is accompanied with an abrupt change in resistivity.

Both models of resistivity were fitted as the logarithm of resistivity. The growth constant was fitted to a value $\alpha = 0.05 \pm K^{-1}$ above and below the phase transition, while the activation energies were found to differ on each side of the phase transition with $E_a = 0.42 \pm 0.04\, eV$ below and $E_a = 0.72 \pm 0.08 eV$ above the transition, respectively. These values of activation energies are of the same order of magnitude as the values reported in the literature for Cu-Cl boracite, although we observe the higher activation energy above T_C. Additionally, they are also of the same order as the one reported for the temperature dependence of the electronic conductivity driven by charge transfer between Cu^{+} and Cu^{2+} in a halide double perovskite[5]

Both fits give reasonably good agreement factors, making it difficult to draw conclusions regarding the most likely physical mechanism for the change in DC conductivity based only on these.

Considering the physics at hand, with an optical bandgap larger than 4 eV and the observation of defect states in the band gap, defect-mediated charge transport could seem to be the more likely mechanism for the observed thermal evolution of the resistivity. However, below the phase transition, charged domain walls were shown to play an important role in the resistivity of the sample. We hypothesize that below the phase transition, both defects and charged domain walls contribute to the resistivity. In this case, the apparent reduction in activation energy that would not be expected for the sole contribution of point defects would stem from the domain wall contribution.

References

1. Schmid, H. & Petermann, L. A. Dielectric constant and electric resistivity of copper chlorine boracite, Cu3B7O13Cl (Cu-Cl-B). *phys. stat. sol.* **41**, K147 (1977).
2. Eliseev, E. A., Morozovska, A. N., Svechnikov, G. S., Gopalan, V. & Shur, V. Y. Static conductivity of charged domain walls in uniaxial ferroelectric semiconductors. *Phys. Rev. B - Condens. Matter Mater. Phys.* **83**, 1–8 (2011).
3. Nataf, G. F. *et al.* Domain-wall engineering and topological defects in ferroelectric and ferroelastic materials. *Nat. Rev. Phys.* **2**, 634–648 (2020).
4. Liu, S. *et al.* Ferroelectric domain wall induced band gap reduction and charge separation in organometal halide perovskites. *J. Phys. Chem. Lett.* **6**, 693–699 (2015).
5. Connor, B. A. *et al.* Alloying a single and a double perovskite: a Cu +/2+ mixed-valence layered halide perovskite with strong optical absorption . *Chem. Sci.* **12**, 8689–8697 (2021).