# Dielectric Relaxation

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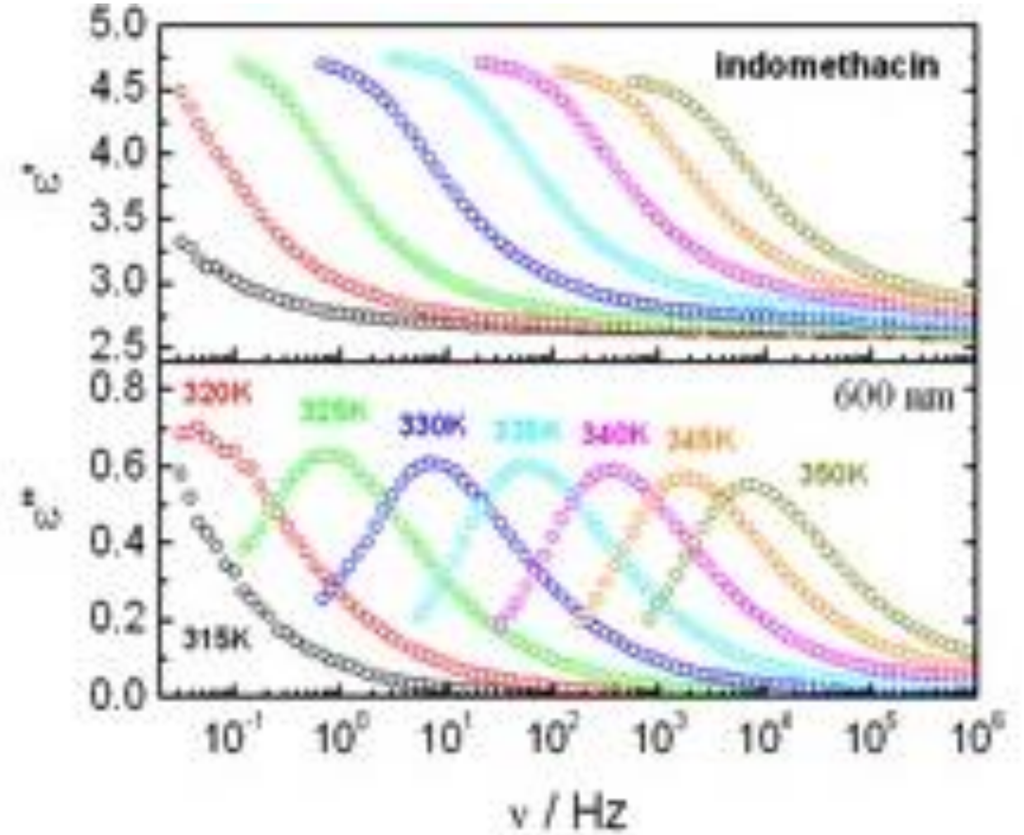
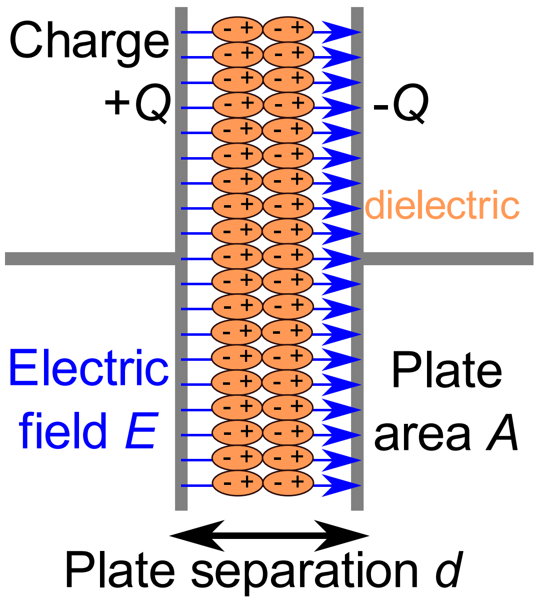
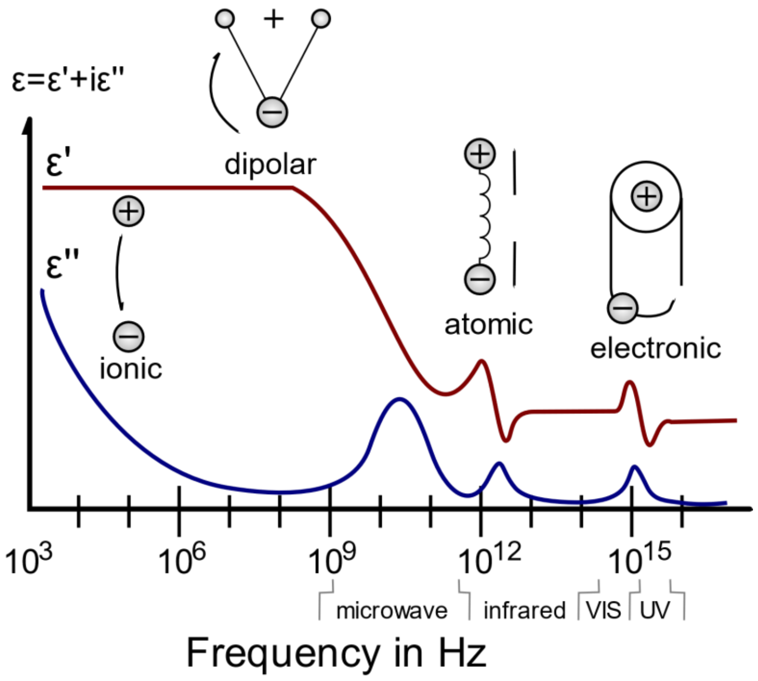


- **Dielectric material** is an electrical insulator that can be polarized by an applied electric field. When a dielectric material is placed in an electric field, **electric charges do not flow through the material** as they do in an electrical conductor but **only slightly shift from their average equilibrium positions causing dielectric polarization.**




- **Dielectric relaxation** is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium.

- Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields



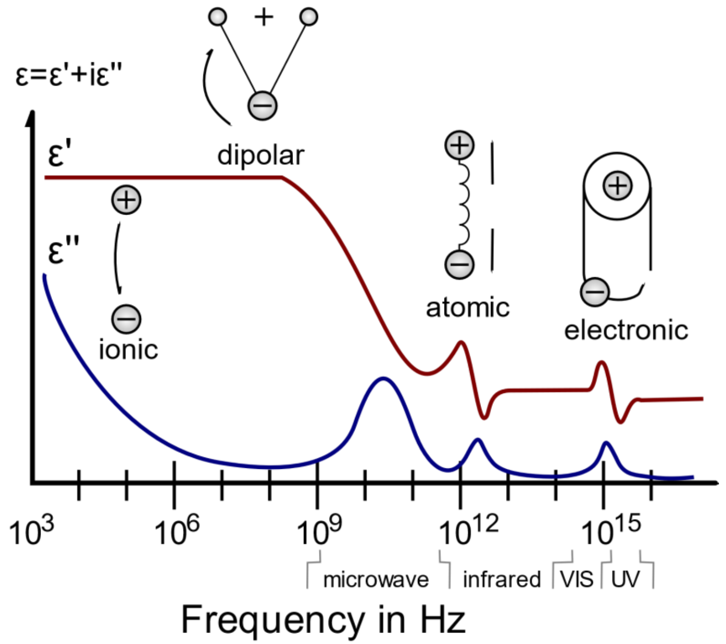
# Debye relaxation

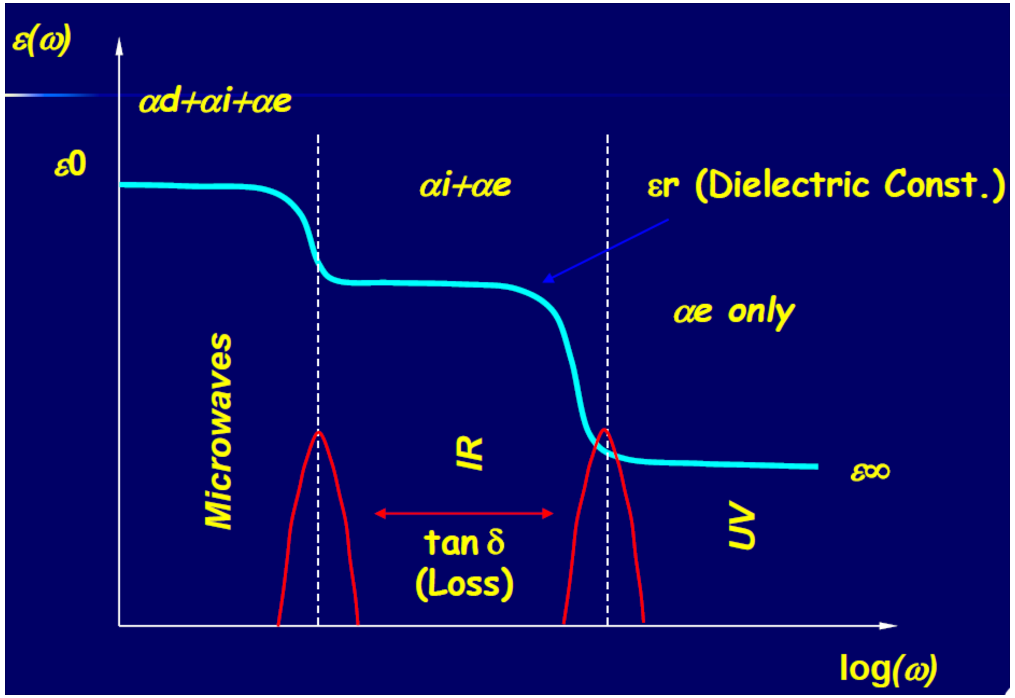
Intrinsic, Permanent dipole moment

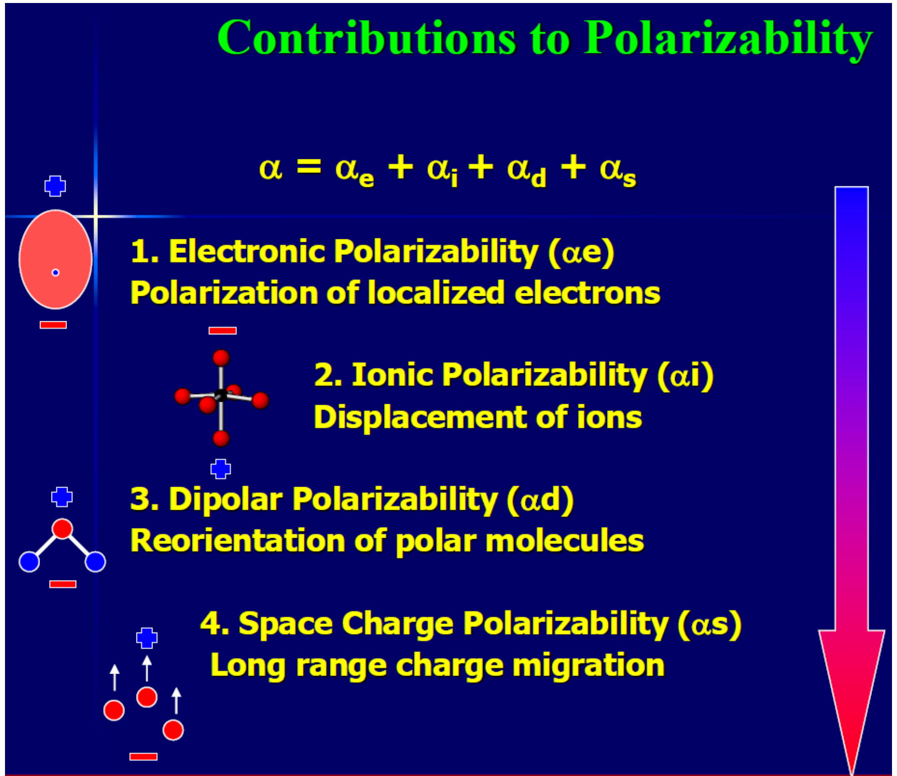
$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\alpha}$$

where $\varepsilon_\infty$ is the permittivity at the high frequency limit, $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ where $\varepsilon_s$ is the static, low frequency permittivity, and $\tau$ is the characteristic relaxation time of the medium. α is a constant with values between 0 and 1.

For an ideal Debye relaxation α=1. α<1 implies that the relaxation has a distribution of relaxation times.



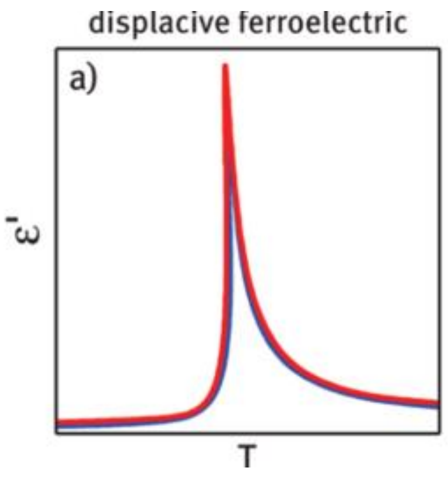



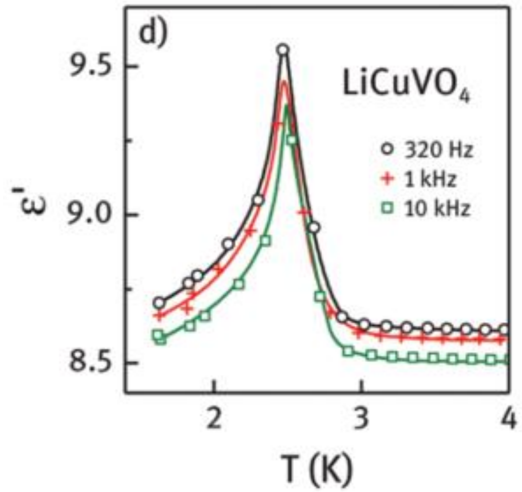




Response time increase

# Signatures of ferroelectricity in dielectric spectroscopy

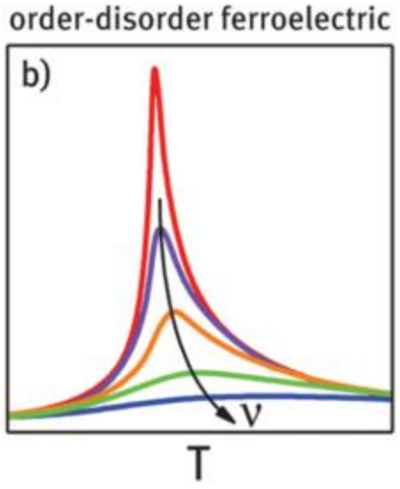
- For **displacive ferroelectric**, at ferroelectric transition, a **high-symmetry structure without permanent dipole moments transfers into a lower symmetry structure with polar order**.
- Usually **no significant frequency dependence of ε′** is observed for this class of ferroelectrics, typically covering frequencies in the Hz–MHz range.

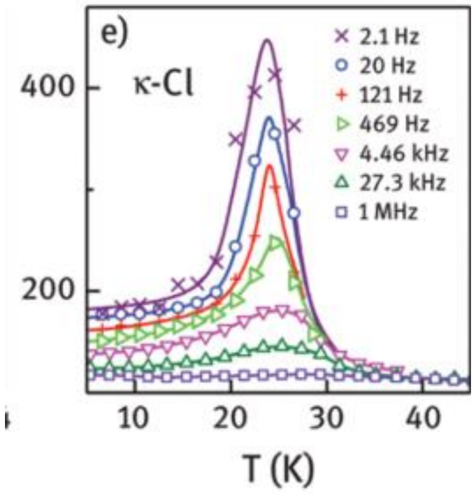



**Improper ferroelectric**, where the polar order is driven by complex magnetic ordering via the inverse Dzyaloshinskii–Moriya interaction

- For **order–disorder ferroelectrics**, **permanent dipole moments already exist above $T_{FE}$**., in the paraelectric state these dipoles are statistically disordered with respect to site and time, but at the ferroelectric transition they align, and polar order arises.




κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl

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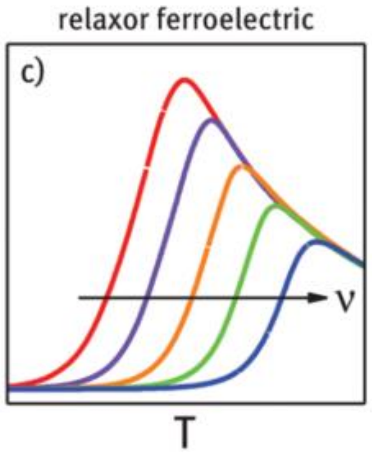
# Signatures of ferroelectricity in dielectric spectroscopy

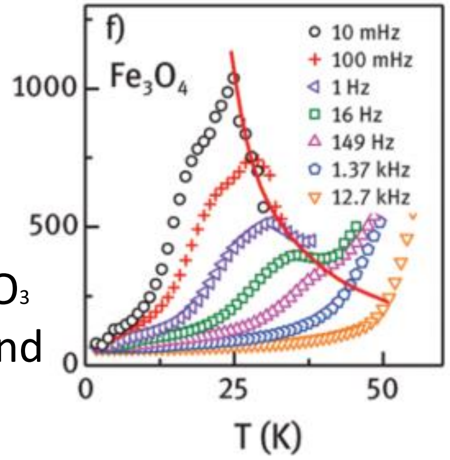
**The relaxor-ferroelectrics**, which roughly can be regarded as ferroelectrics with **a smeared-out phase transition**.

Vogel–Fulcher–Tammann (VFT) law

$$\tau = \tau_0 \exp\left[\frac{B}{T - T_{VF}}\right]$$

$T_{VFT}$ is the divergence temperature of τ, where the dipolar dynamics finally becomes frozen, and B is an empirical constant.

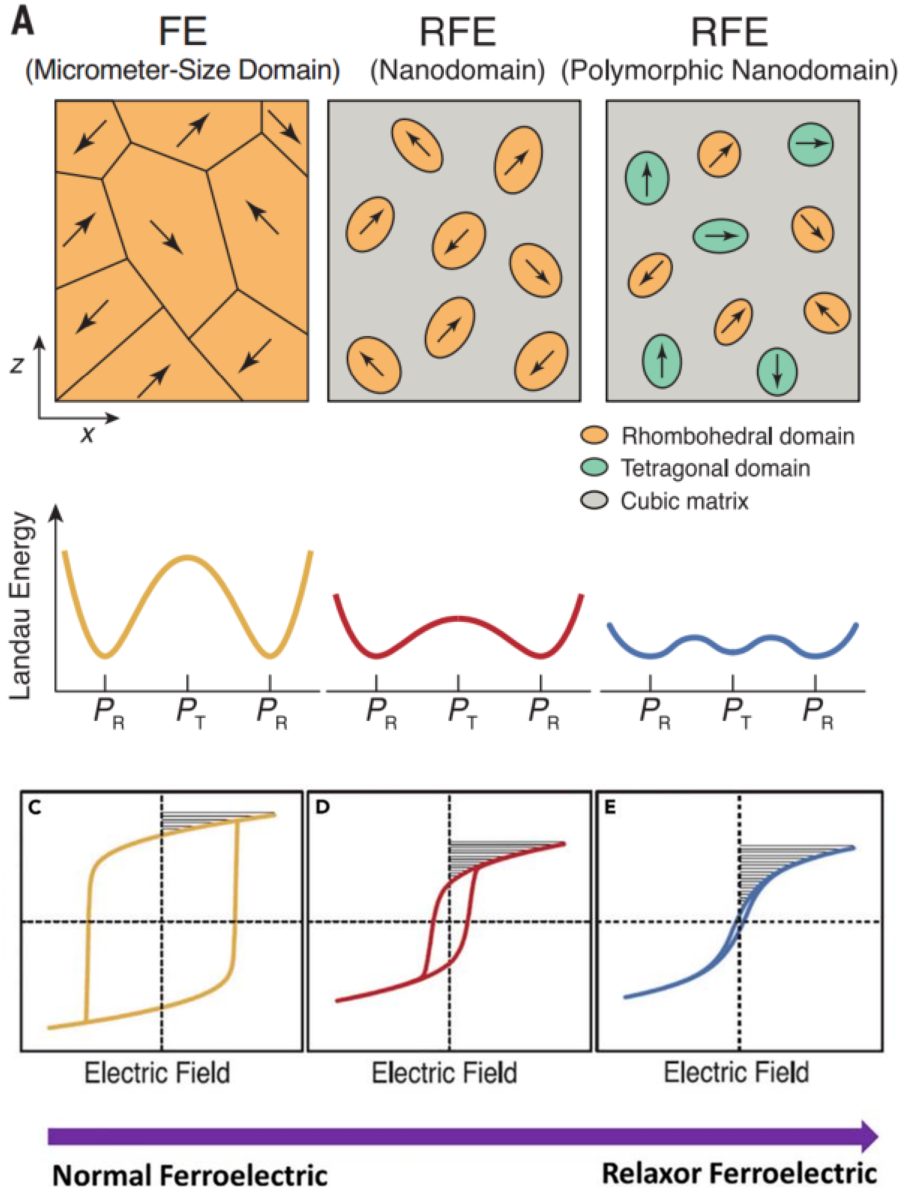



Typical example of canonical RF is the $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) systems where the non-isovalent ions $Mg^{2+}$ and $Nb^{5+}$ are fully or partially disordered on the B-site.

The VFT behavior in RF is interpreted as a consequence of the formation, growing and cooperative reaction between the polar nanoregions (PNRs).

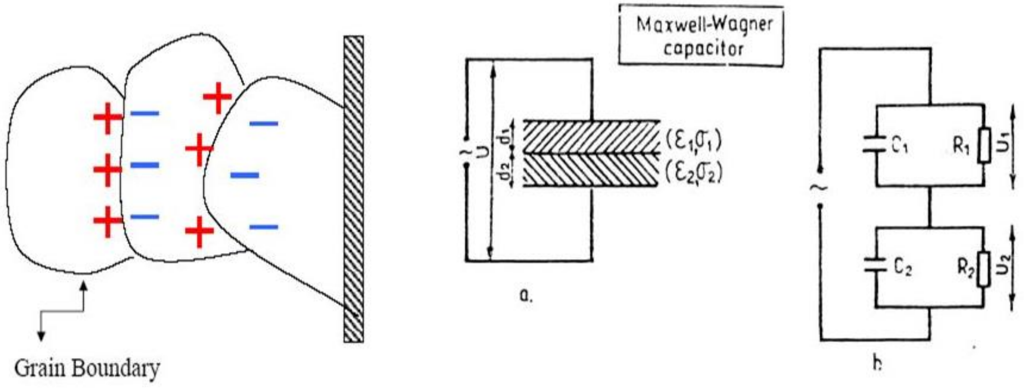
**Disorder helps promoting relaxor-ferroelectric states.**




Science 365, 578–582 (2019)

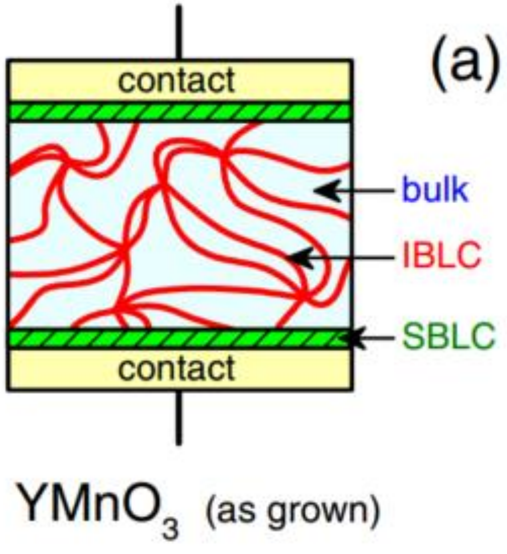
**Maxwell-Wagner relaxation-**Extrinsic effects often occurs in the heterogeneous systems in which the component dielectrics have different conductivities

For example, grain boundaries and/or the electrodes applied to the sample can produce the effect.



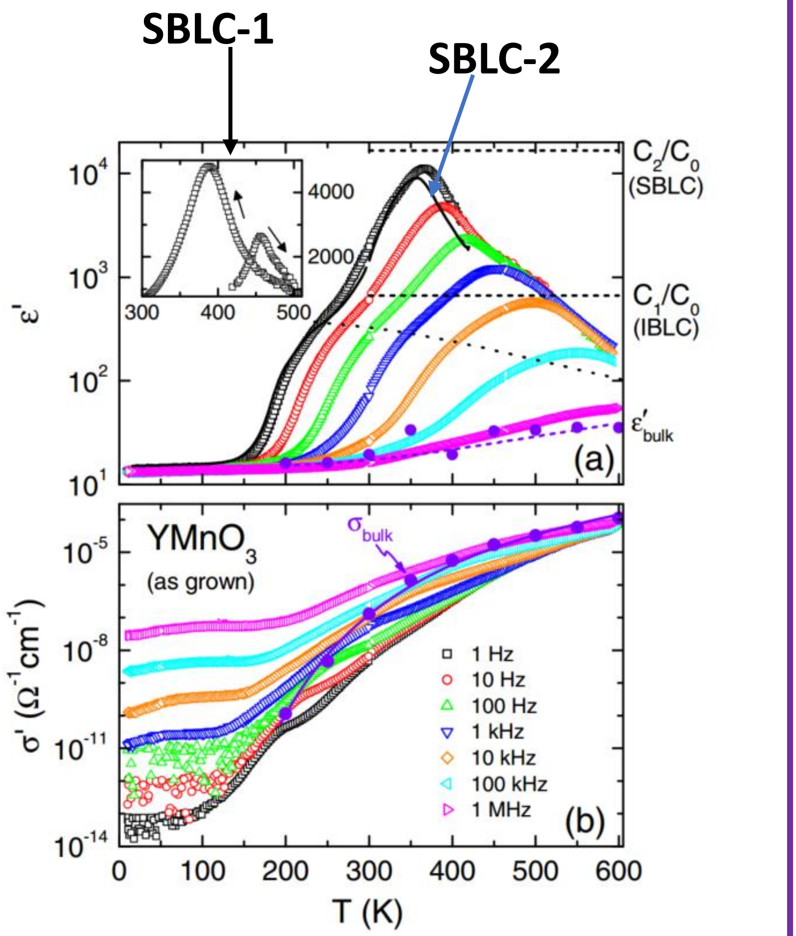

Thinner capacitor with larger capacitance

**This can lead to so-called MW relaxations, non-intrinsic effects that should not be confused with the intrinsic relaxational response found in order–disorder or relaxor-ferroelectrics.**




**$\varepsilon'_{bulk} \approx 20$**

PRL 118, 036803 (2017)




**Surface-barrier layer capacitor (SBLC):** non-intrinsic and irreproducible
1.A change of the oxygen stoichiometry (300 K - 600 K) at the sample surface seems a reasonable explanation for this phenomenon.
2. Schottky diodes forming when metallic electrodes are applied to semiconducting samples (change the top electrodes)
**Internal barrier layer capacitors (IBLCs)** : Reproducible
Grain boundaries with low conductivity.

# A simple example

The total admittance (complex conductance) of a single RC circuit is $Y = G + iC$

$$Y_{tot} = G'_{\mathrm{tot}} + iG''_{\mathrm{tot}} = \frac{Y_l Y_b}{Y_l + Y_b} = \frac{(G_l + i\omega C_l)(G_b + i\omega C_b)}{G_l + G_b + i\omega(C_l + C_b)}$$

$$C'_{\mathrm{tot}} = \frac{(G_l^2 C_b + G_b^2 C_l) + \omega^2 C_l C_b (C_l + C_b)}{(G_l + G_b)^2 + \omega^2 (C_l + C_b)^2}$$

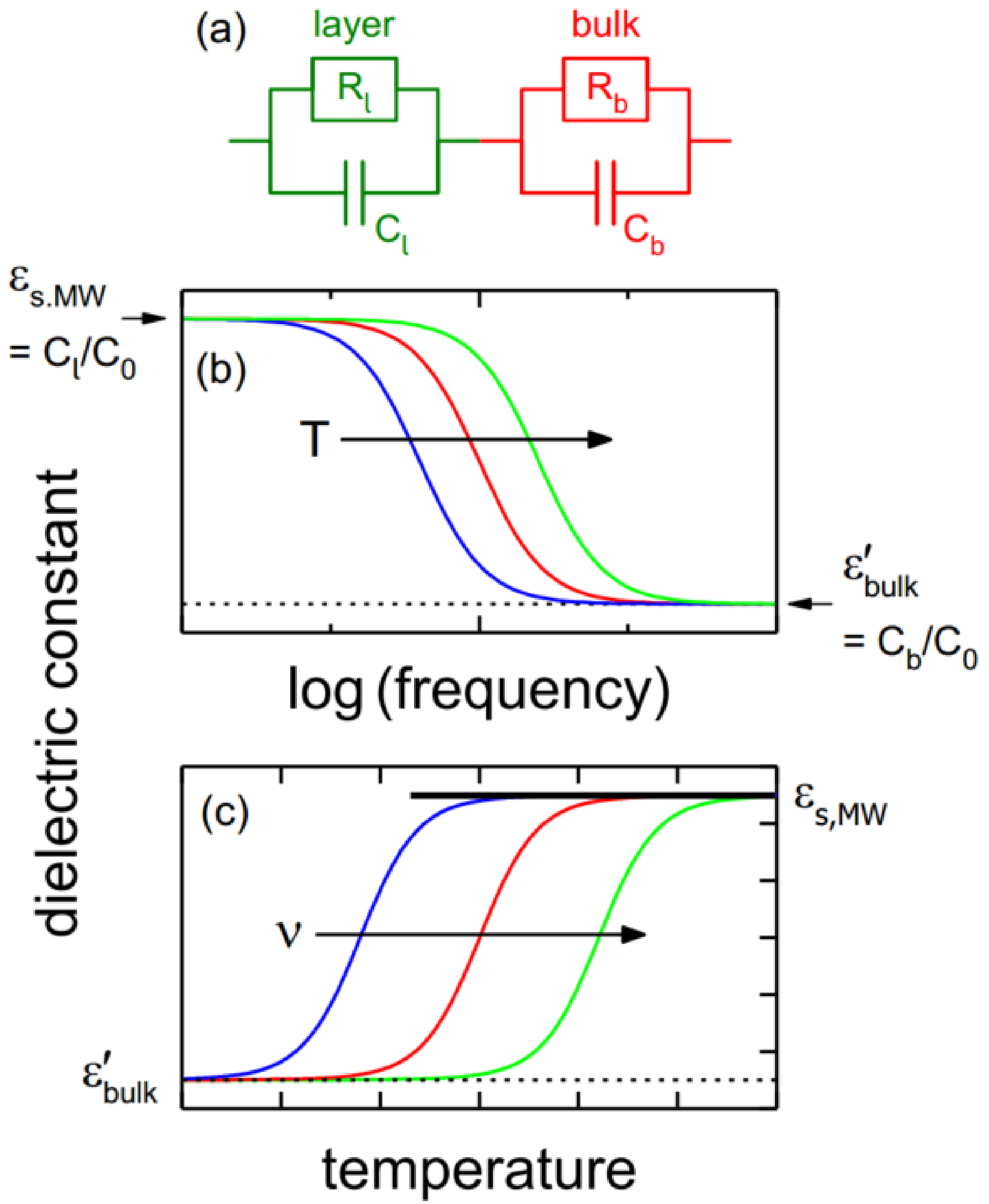
$$\nu \to 0, \quad C_{s,\mathrm{MW}} = \frac{G_l^2 C_b + G_b^2 C_l}{(G_l + G_b)^2}$$

$G_l$ « $G_b$ and $C_l$ » $C_b$

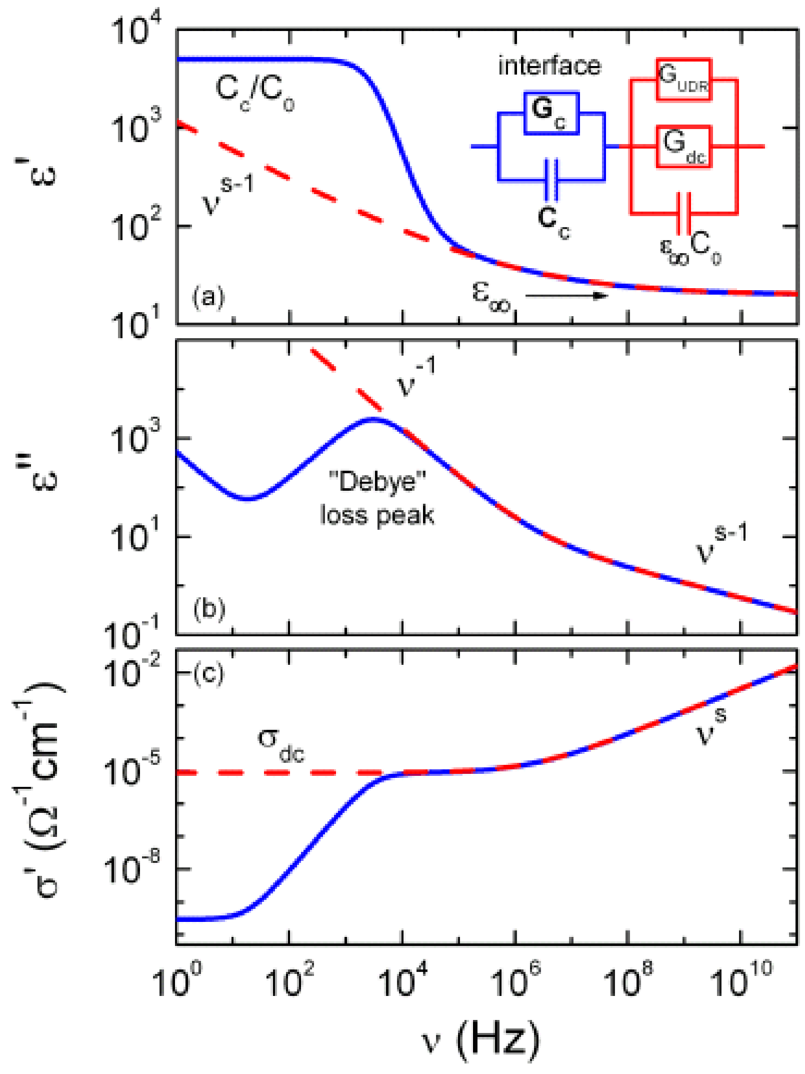
$$C_{s,\mathrm{MW}} = C_l \text{ and } \varepsilon_{s,\mathrm{MW}} = C_l/C_0$$

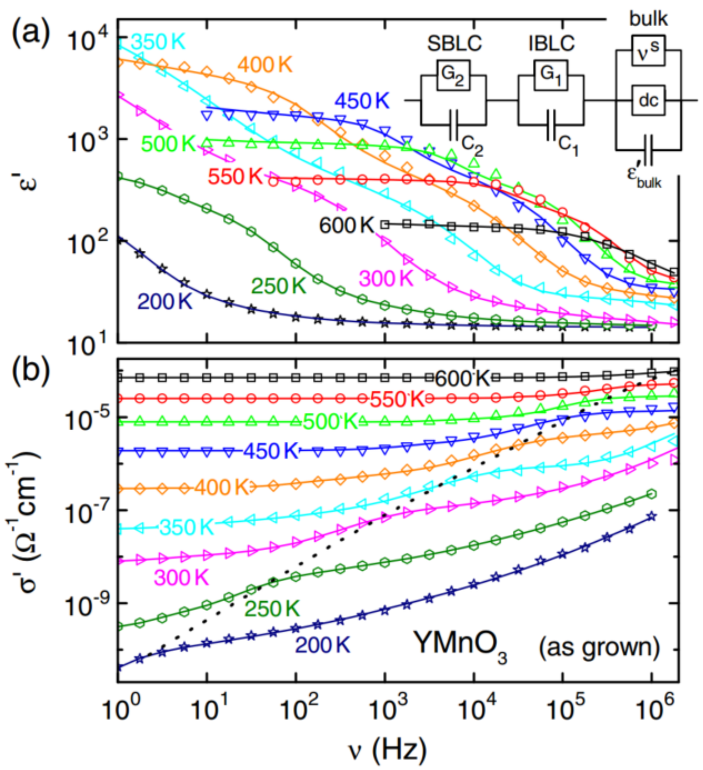
For this scenario, obviously the **layer properties** completely dominate the detected dielectric response at low frequencies or high temperatures

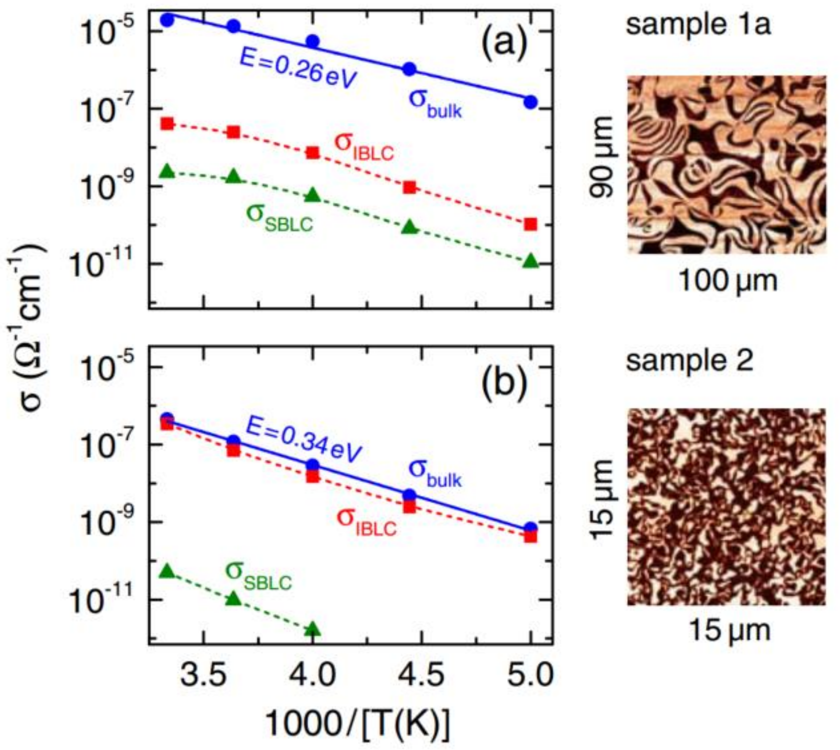
In contrast, at high frequencies or low temperatures, the response is dominated by the **bulk properties** because, with increasing frequency (or decreasing temperature)



# More complex case

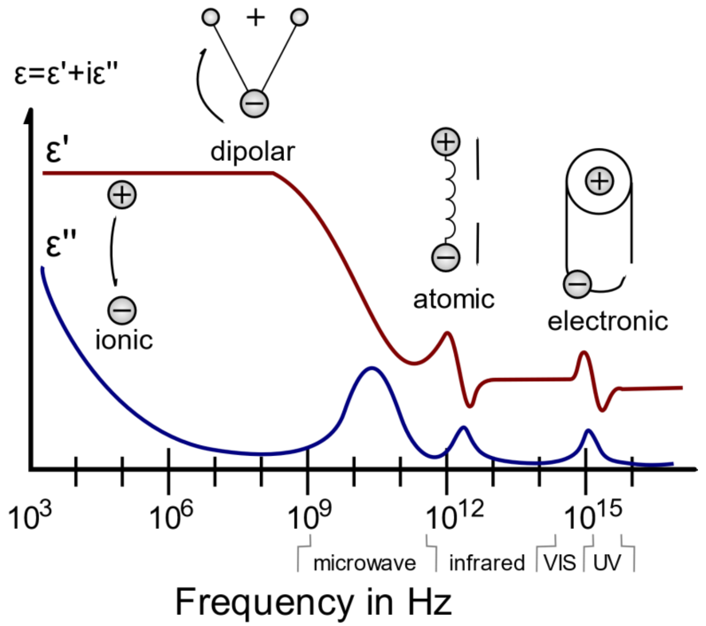


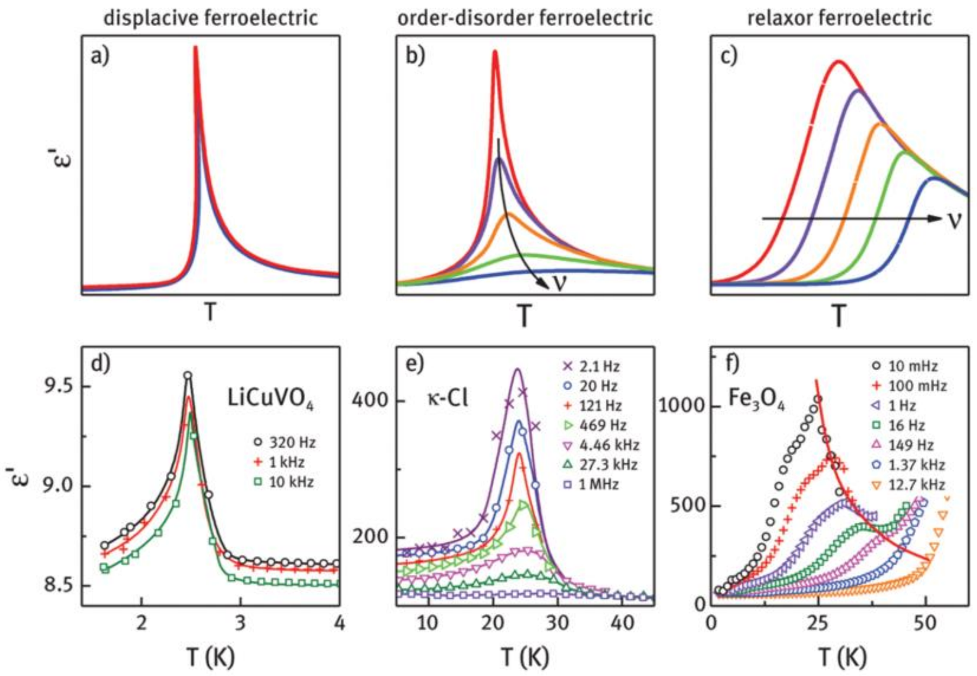



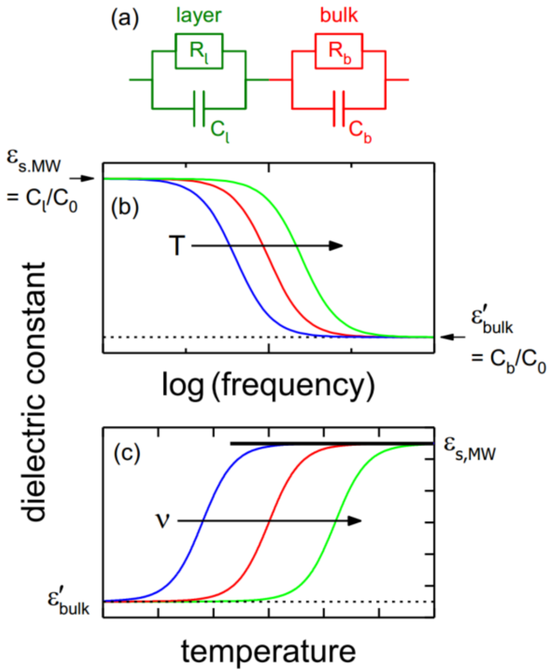



# Summary

## Dielectric relaxation




**Debye relaxation**

**Phase transition**

**Maxwell-Wagner relaxation**