Secondary pyroelectric and electrocaloric effects in epitaxial PZT layers

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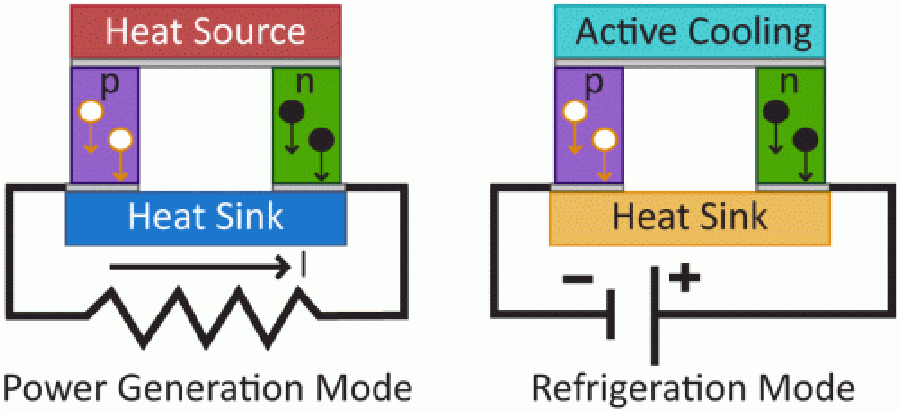
supported by ONR and AFOSR

Outline

- The big picture: where can we find large entropy changes in solid state or condensed matter systems?
- Our recent contribution: measurements of the pyroelectric and electrocaloric coefficients of thin epitaxial layers
  - Wide frequency range (1 Hz to 10 MHz) pyroelectric coefficients reveal secondary effects. No evidence of extrinsic (domain wall motion) contributions.
  - Comparison of electrocaloric and pyroelectric coefficients reveal importance of changes in vibrational entropy.

Solid state heat engines have to compete with the entropy of the lattice vibrations

- Thermoelectrics use the entropy per charge carrier per unit charge (i.e., the Seebeck coefficient) to pump heat or generate power from a temperature gradient.
  - Unfortunately, lattice vibrations dominate the heat current and the part of the heat current carried by the lattice vibrations is wasted.



http://www.eng.utah.edu/~sparks/how-do-thermoelectrics-work.html

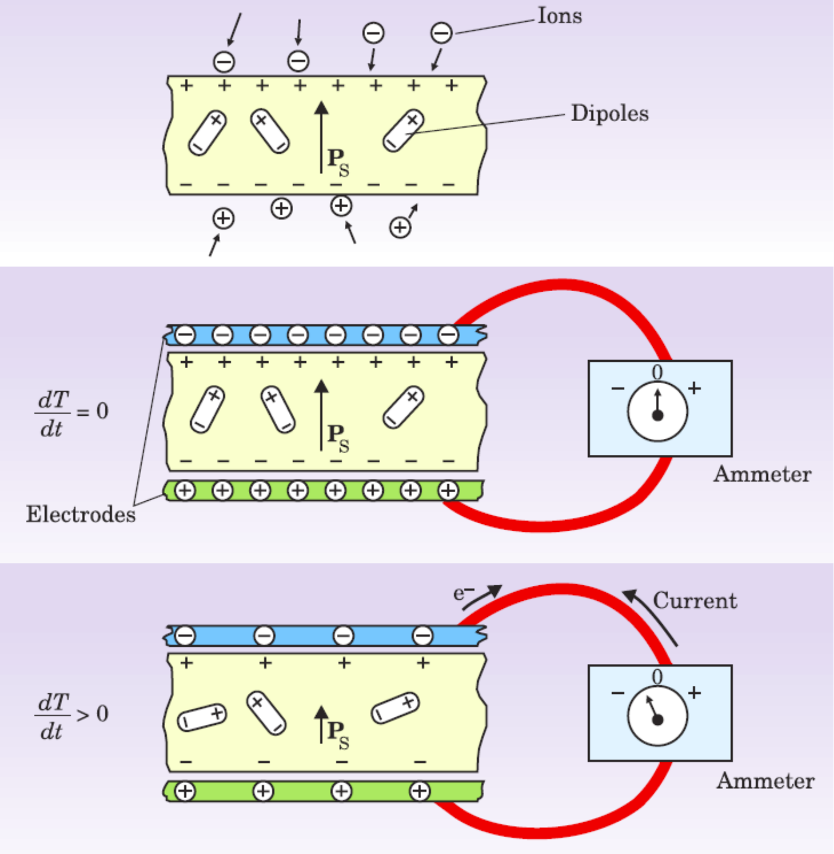
Solid state heat energies have to compete with the entropy of the lattice vibrations

- In pyroelectric (generate electrical power from temperature excursion) or electrocaloric (pump heat using electric fields) materials, the entropy associated with the electrical polarization has to compete with the entropy of the lattice vibrations.

- Hard to match liquid-vapor systems because the change in configurational entropy of the vapor is large.

- An example of a “log” problem. Entropy is $k_B \ln$(# of configurations). Hard to make a big change in the function ln(x).

Do schematics of thermally disordered dipoles capture the essential physics?



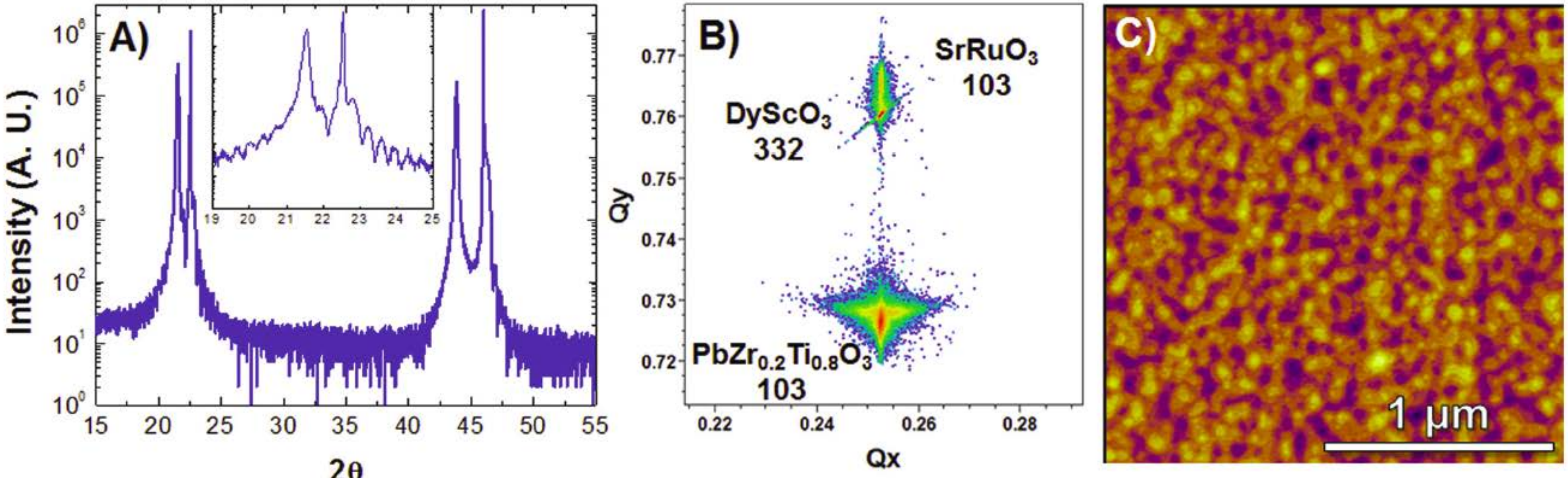
Lang, *Physics Today* (2005)

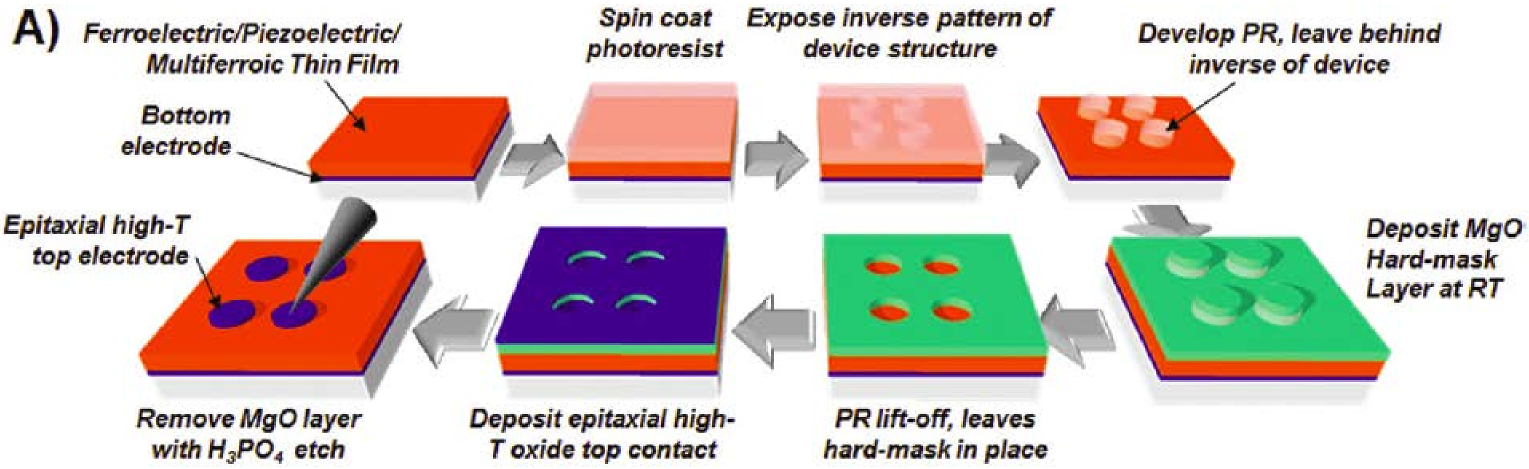
- Our conclusion: changes in the entropy of the lattice vibrations due to changes in the vibrational spectrum are also important.

Epitaxial growth of ferroelectric oxides by pulsed laser deposition.

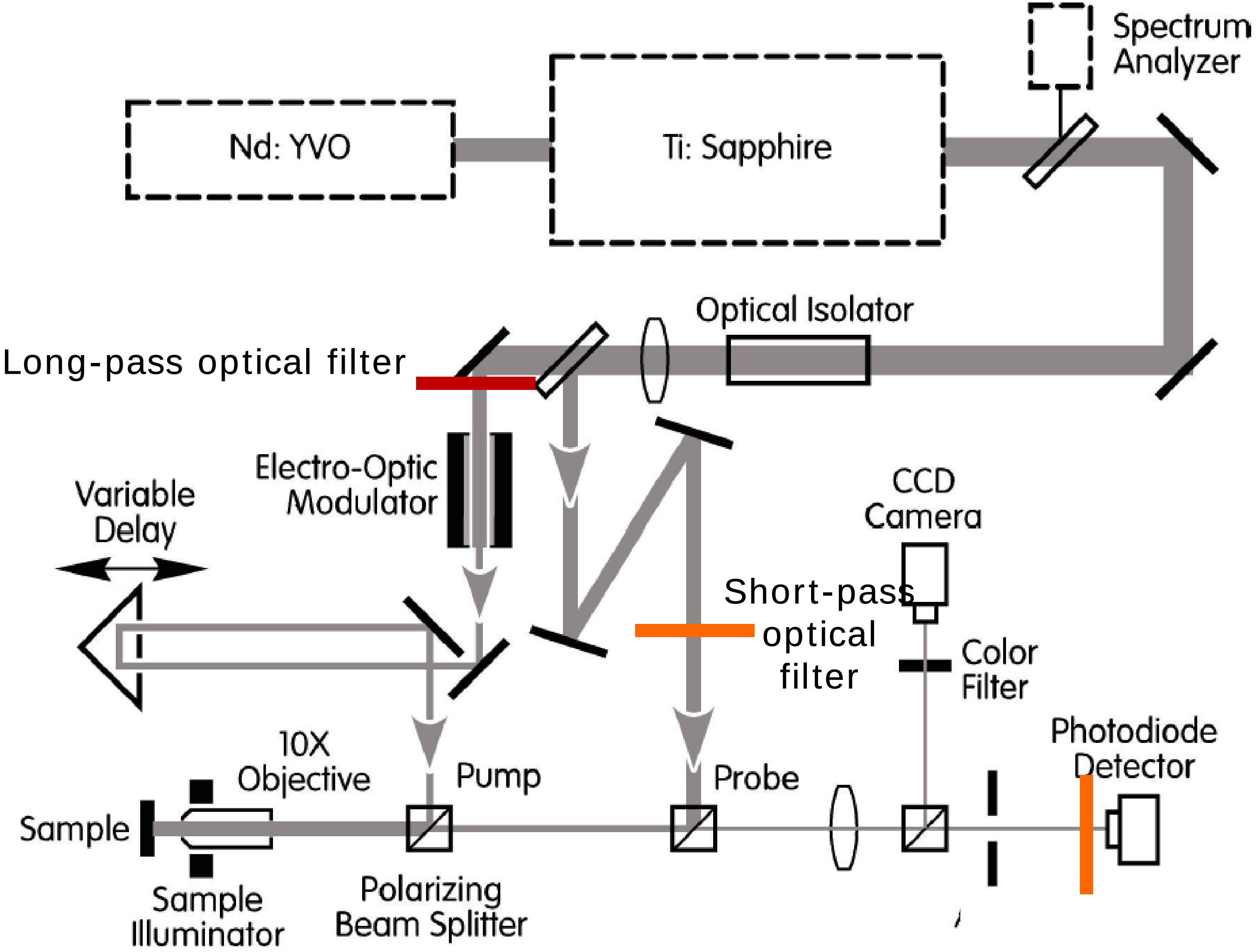
- $SrRuO_3$/PZT/$SrRuO_3$ capacitor structure on $DyScO_3$ substrate

Karthik et al., Advanced Materials (2012)





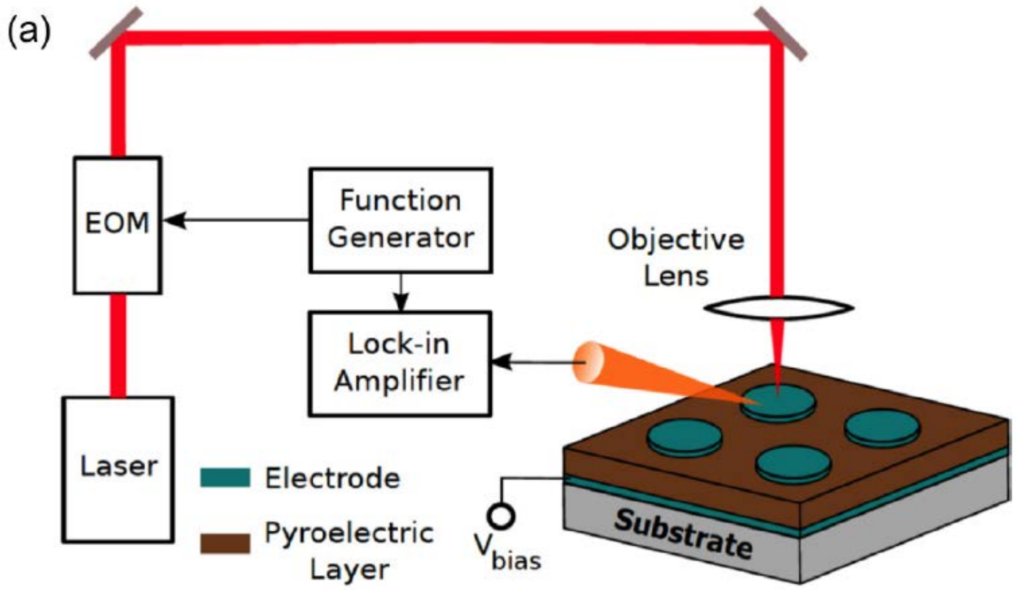
Time-domain thermoreflectance to measure thermal conductivity

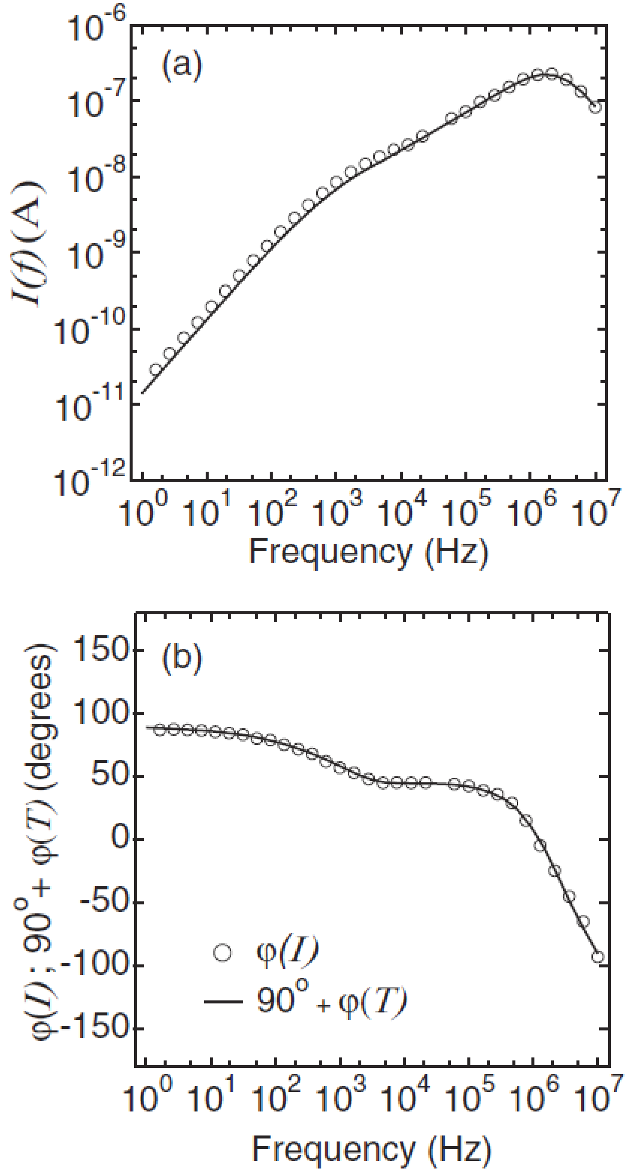


Kang *et al*., RSI (2008)

I. Wide frequency range pyroelectric measurements, 1 Hz to 10 MHz

- Experiment and modeling using a constant value of the pyroelectric coefficient.

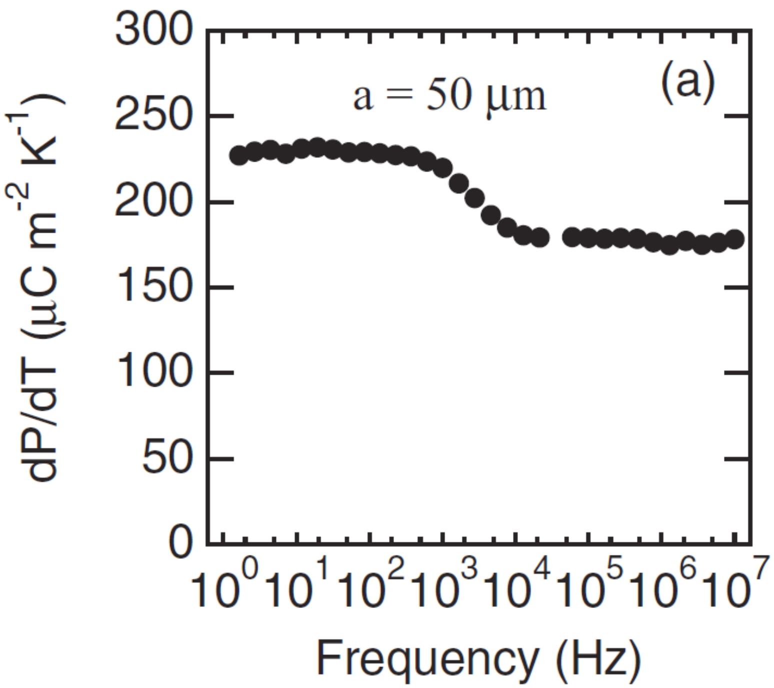




Tong et al., Phys. Rev. B (2014)

No evidence in these data for (or against) extrinsic effects, i.e., domain wall motion

- Fit pyroelectric coefficient at each frequency.
- Increase at low frequencies is due to the change in mechanical constraints.
  - At high frequency, thermal expansion of the film is constrained laterally by the substrate
  - At low frequency, the biaxial stress is greatly reduced.



Tong et al., Phys. Rev. B (2014)

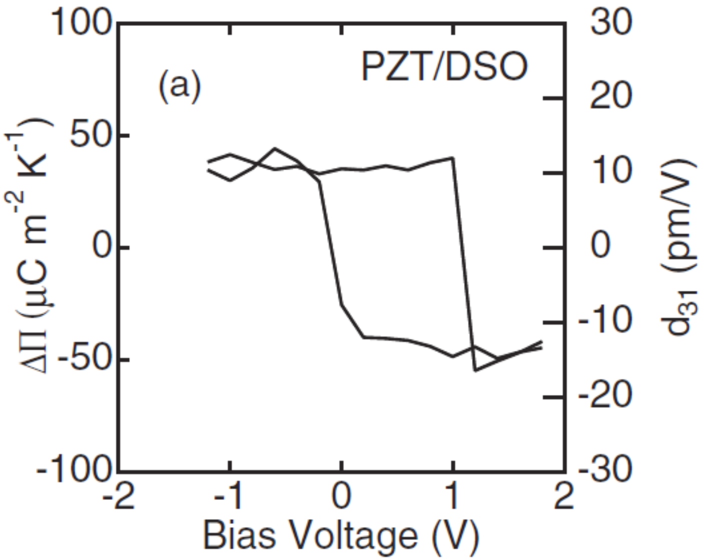
Secondary effects have the same field dependence as the primary effect

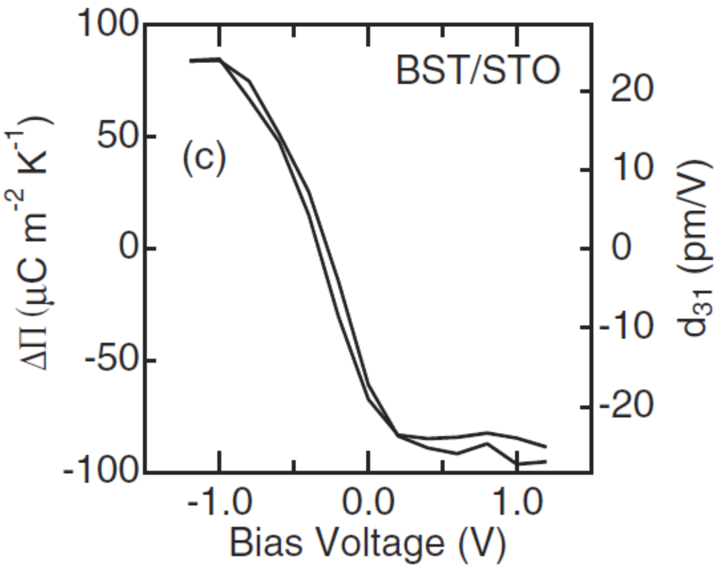
- Plot the difference in high and low frequency pyroelectric coefficients as a function of bias field

High frequency $$\Pi_1 = \Pi - \frac{2d_{31}\alpha_1}{s_{11} + s_{12}}$$

Low frequency $$\Pi_2 = \Pi - \frac{2d_{31}(\alpha_1 - \alpha_{1s})}{s_{11} + s_{12}}$$

$$\Pi_2 - \Pi_1 = 2d_{31}\alpha_{1s}/(s_{11} + s_{12})$$

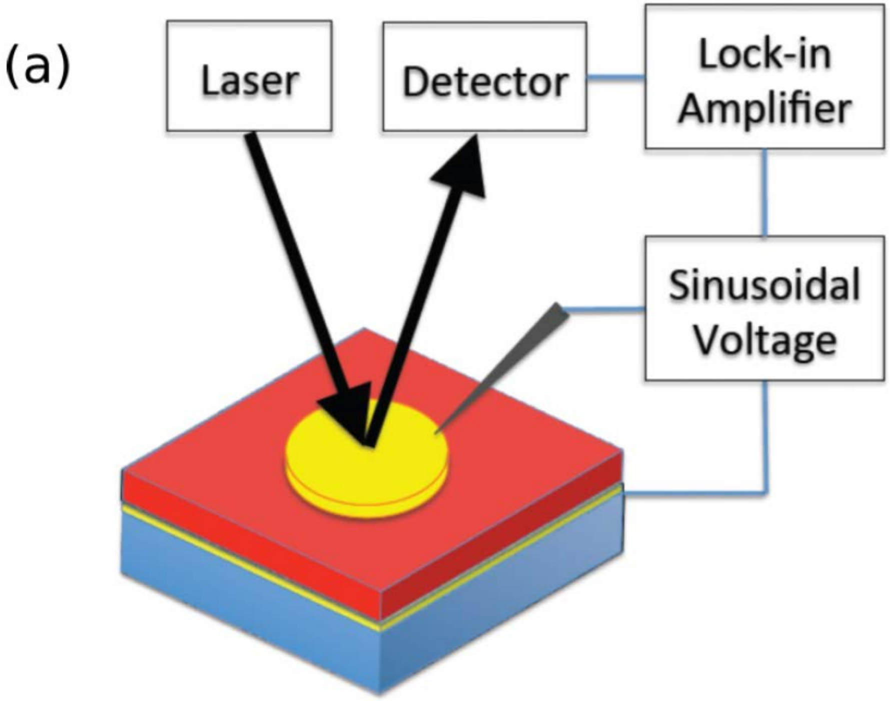




Tong et al., Phys. Rev. B (2014)

II. Direct measurements of electrocaloric coefficients of an epitaxial layer

- Use thermoreflectance (dR/dT) as a high bandwidth (10 MHz), high sensitivity (10 mK Hz$^{-1/2}$) thermometer
- Top contact is vandadium for high dR/dT and compatibility with processing.



Tong et al., Phys. Rev. B (2014)

Electrocaloric Σ and pyroelectric Π coefficients are not equal for a clamped film

- Use thermoreflectance (dR/dT) as a high bandwidth (10

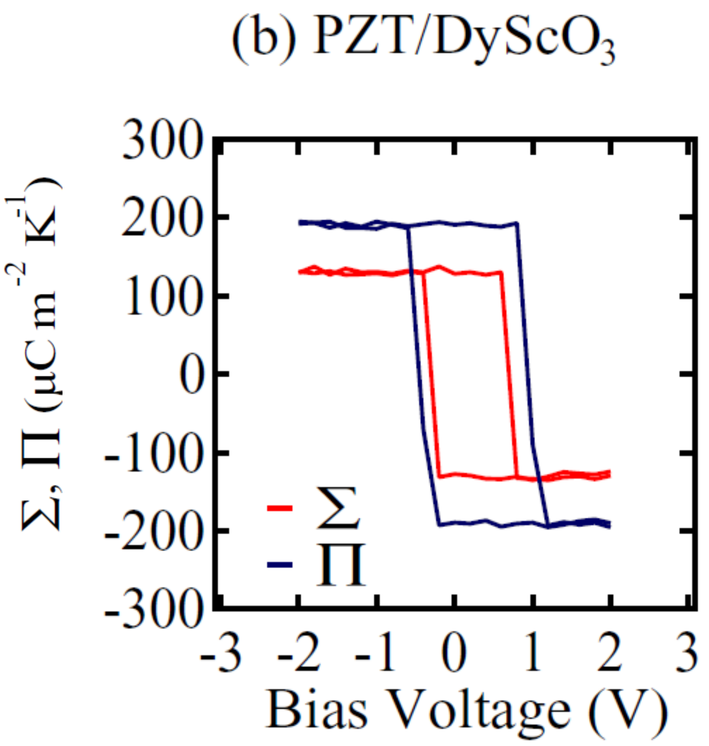
$$\Sigma = \frac{dS}{dE} = \Sigma' + \Sigma''$$

$$\Sigma'' = C(2d_{31}\gamma_1 + d_{33}\gamma_3)$$

$$\Pi = \frac{dP}{dT} = \Pi' + \Pi''$$

$$\Pi'' = d^*_{33}c_{33}\alpha_3$$

$$\Sigma - \Pi = d_{33}(\gamma_3 C - c_{33}\alpha_3) = 2d_{33}c_{13}\alpha_1$$

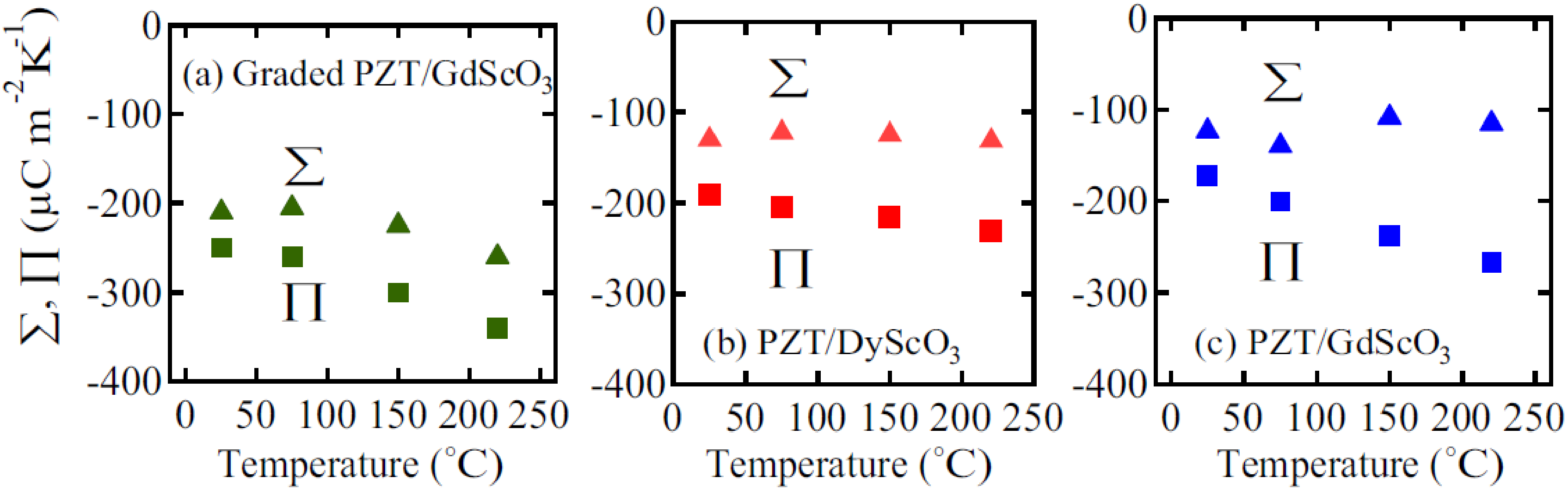


Tong et al., Phys. Rev. B (2014)

For clamped films, the electrocaloric coefficient cannot be predicted from measurements of the pyroelectric coefficient

- At elevated temperatures, secondary effects are of the same order as the primary effects.

$$\Sigma = \frac{dS}{dE} = \Sigma' + \Sigma'' \qquad \Pi = \frac{dP}{dT} = \Pi' + \Pi''$$



Tong et al., Phys. Rev. B (2014)

Summary

- Difficult to get large entropy changes in condensed matter systems.

$$\frac{\Sigma(\Delta E)}{C} \approx \frac{(3\times10^{-4})(10^{8})}{(3\times10^{6})} \approx 10^{-2}$$

- Significantly advanced experimental methods for probing electrocaloric coefficients in thin epitaxial layers
  - Enables exploration of effects of static strain, composition gradients, metastable structures and compositions.
  - For clamped films (zero in-plane strain), pyroelectric and electrocaloric coefficients are significantly different due to the large magnitude of secondary effects.
- Changes in vibrational entropy with electrical field and strain are important to consider and may provide a route to higher efficiency materials for pyroelectric/electrocaloric energy conversion.