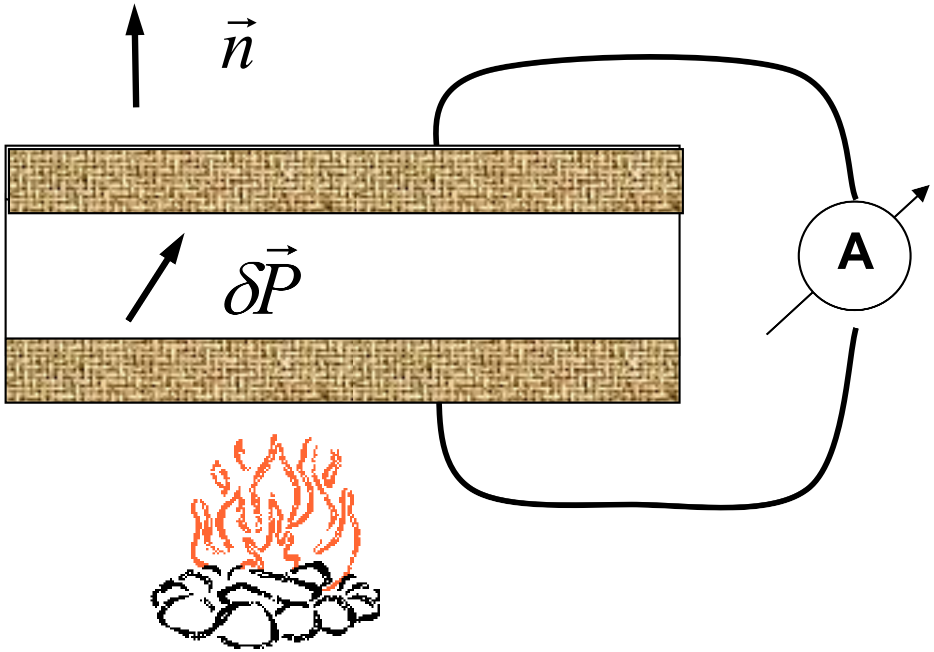
Lecture 7-2 (weeks 7-8, 1-6 April 2025)

Thermo-Electro-mechanics

- Pyroelectricity and thermal expansion
- General description of electro-thermo-mechanical response

Pyroelectricity



$$\delta T \Rightarrow \delta Q$$

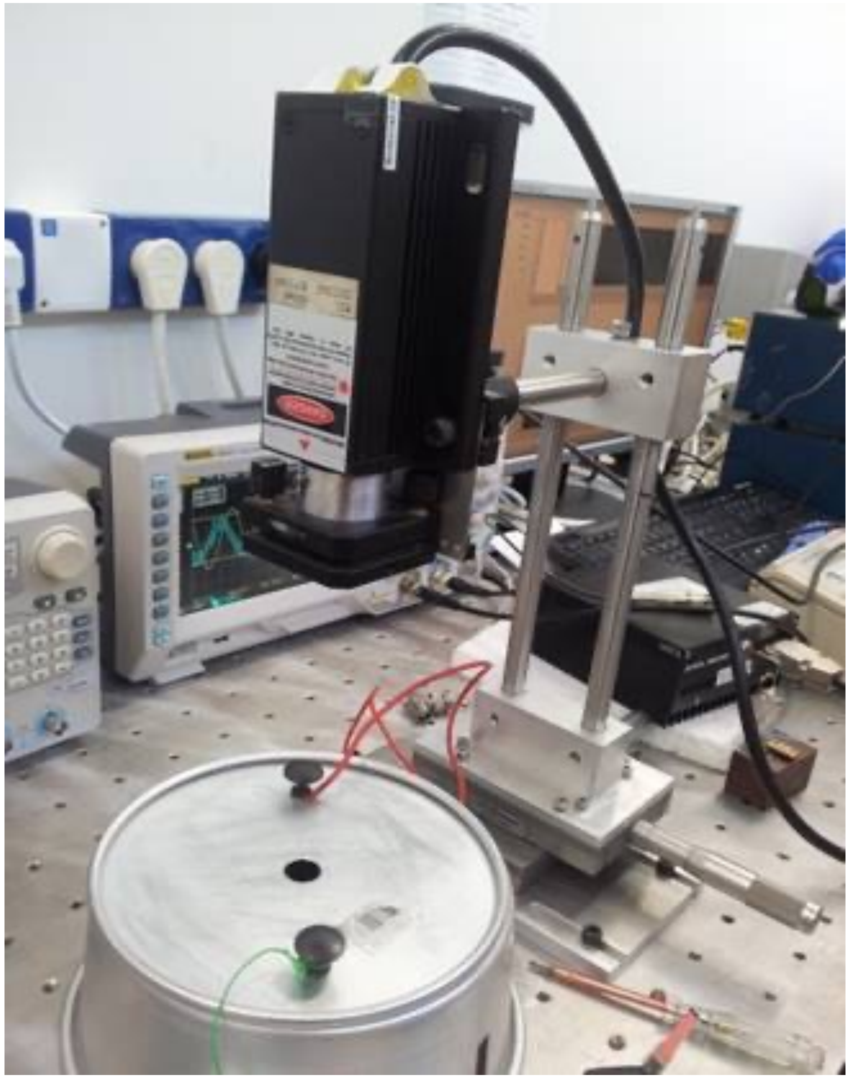
$$\boxed{\vec{E} = 0}$$

$$\delta Q = S \cdot \delta\sigma \qquad \delta\sigma = \delta\vec{D} \cdot \vec{n} \qquad \delta D_i = \delta P_i = \left(\frac{\partial P_i}{\partial T}\right)_{E=0} \delta T$$

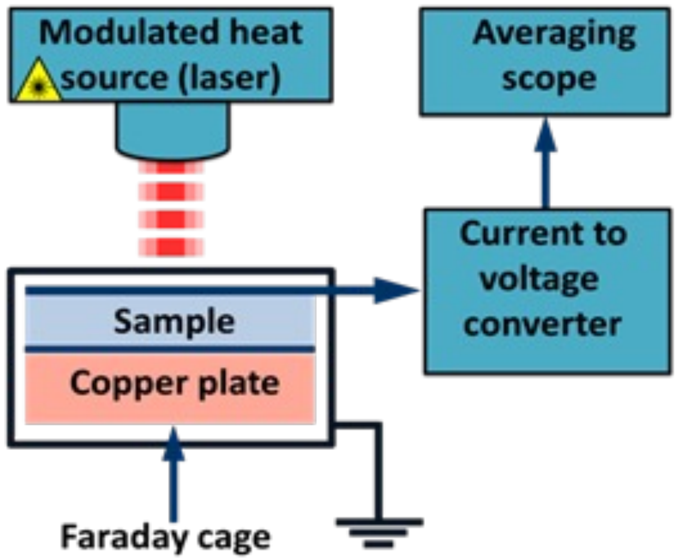
S **electrode area**

$$p_i = \left(\frac{\partial P_i}{\partial T}\right)_{E=0}$$ **pyroelectric coefficient**

Pyroelectric measurements



$$I(t) = \frac{dQ}{dt} = S * p * \frac{dT}{dt}$$



Pyroelectricity

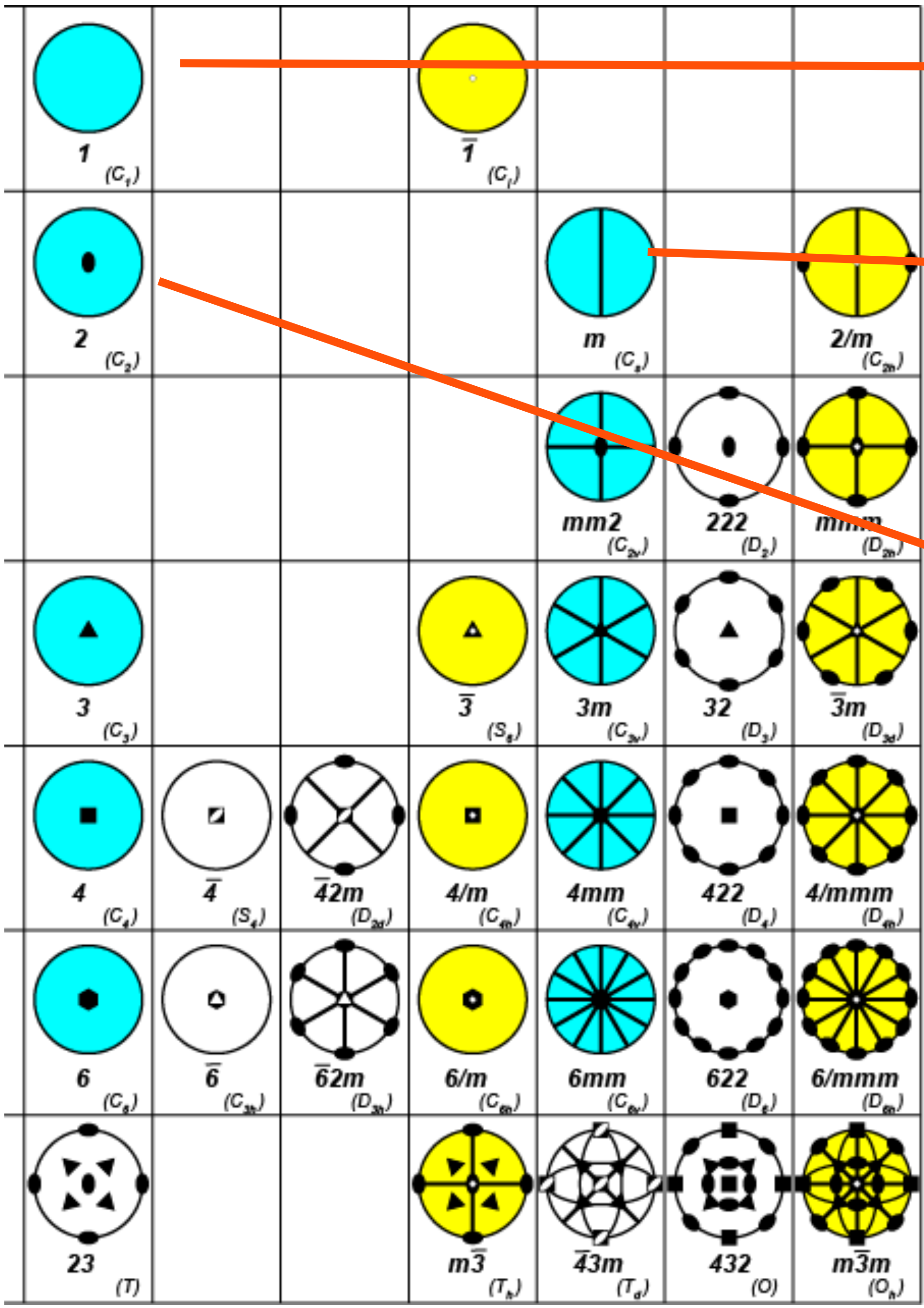
Where is it possible?

$$P_i = p_i \delta T \quad \text{or} \quad D_i = p_i \delta T \quad \text{at} \quad E_i = 0$$

One needs an invariant vector

One needs a polar group since in polar groups there exists a direction that cannot be changed by the symmetry operations of the material (this is a direction for the invariant vector)

Pyroelectric: only blue and $\infty, \infty m$



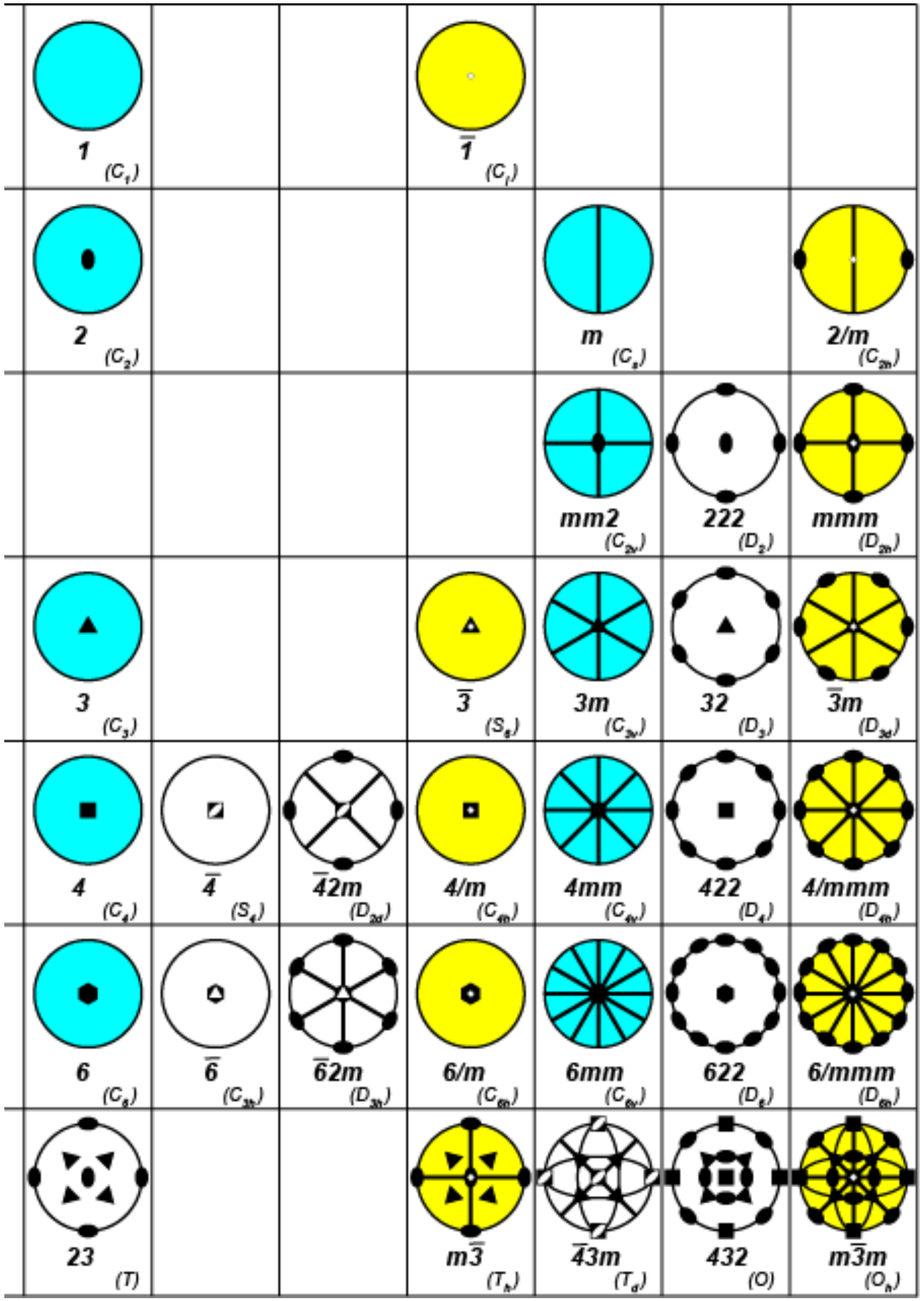
$\begin{pmatrix} p_1 \\ p_2 \\ p_3 \end{pmatrix}$ 3

$\begin{pmatrix} p_1 \\ p_2 \\ 0 \end{pmatrix}$ 2 **for** m

$\infty, \infty m$

$\begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix}$ 1

Symmetry of pyroelectric response



$$\begin{pmatrix} 0 \\ 0 \\ p_3 \end{pmatrix} \qquad \infty m$$

Examples of pyroelectric materials

Compare the effects of temperature and electric field on *P*

Tourmaline
(Musée cantonal de géologie, Lausanne)

$3m$

Complex aluminium-borosilicate

How strong is the effect?

$$P_3 = p_3 \delta T$$

$$P_3 = \varepsilon_0 (K_{33} - 1) E_3$$

$$p_3 = 0.4 \text{ nC/cm}^2\text{K}$$

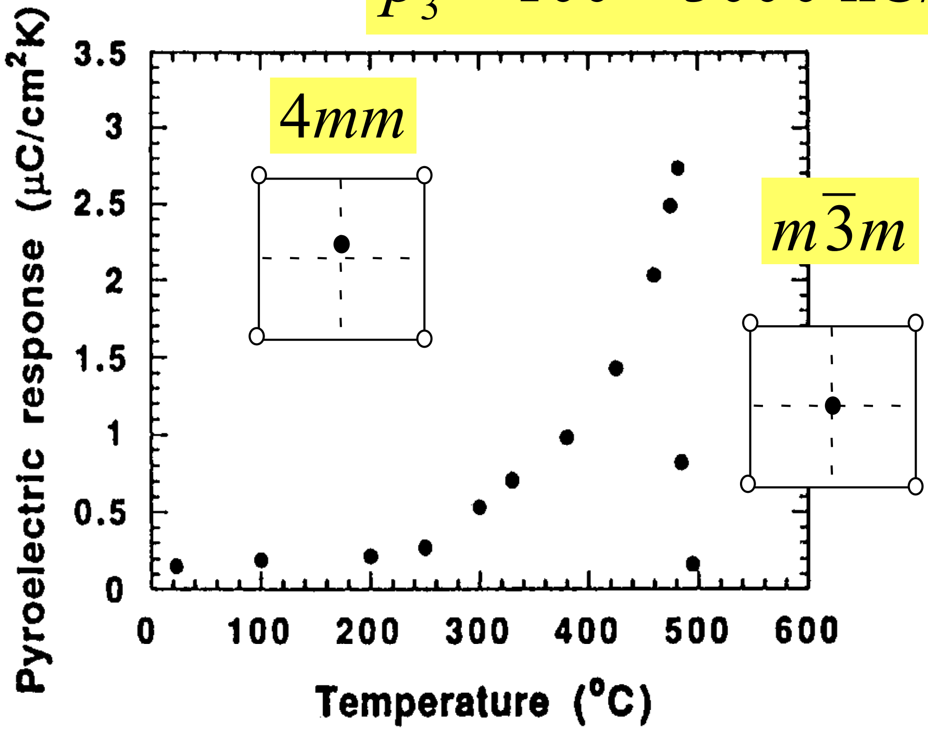
$$K_{33} = 7.1 \qquad \delta T = 1 \text{ K}$$

$$E_{equiv} = p_3 \delta T / \varepsilon_0 (K_{11} - 1)$$

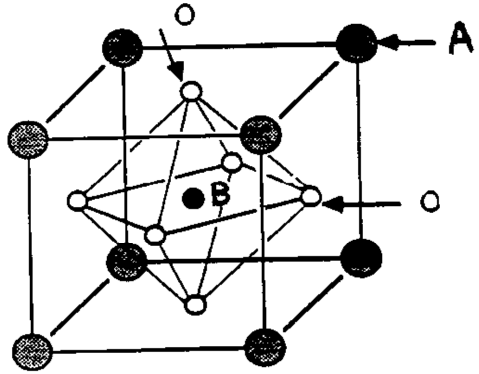
$$\approx 1 \text{ kV/cm}$$

Example- perovskites

$p_3 = 100 - 3000 \text{ nC/cm}^2\text{K}$



$PbTiO_3$



$A = Pb$

$B = Ti$

Temperature sensor for $\delta T < 10^{-3}$-10^{-4} K

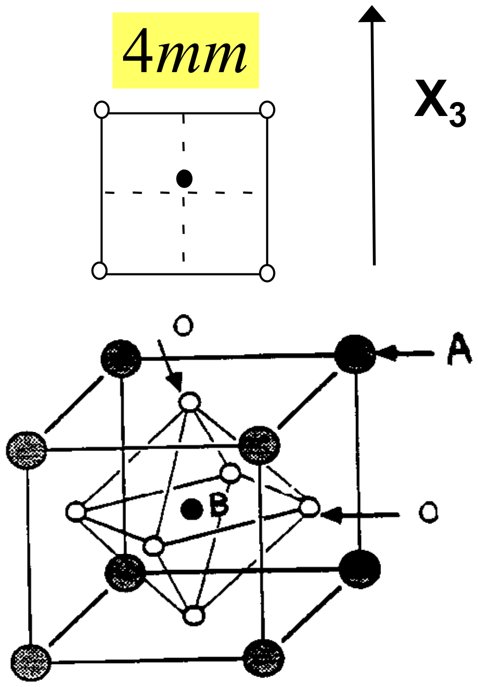
Tourmaline

$p_3 = 0.4 \text{ nC/cm}^2\text{K}$

$Pb(Zr, Ti)O_3$

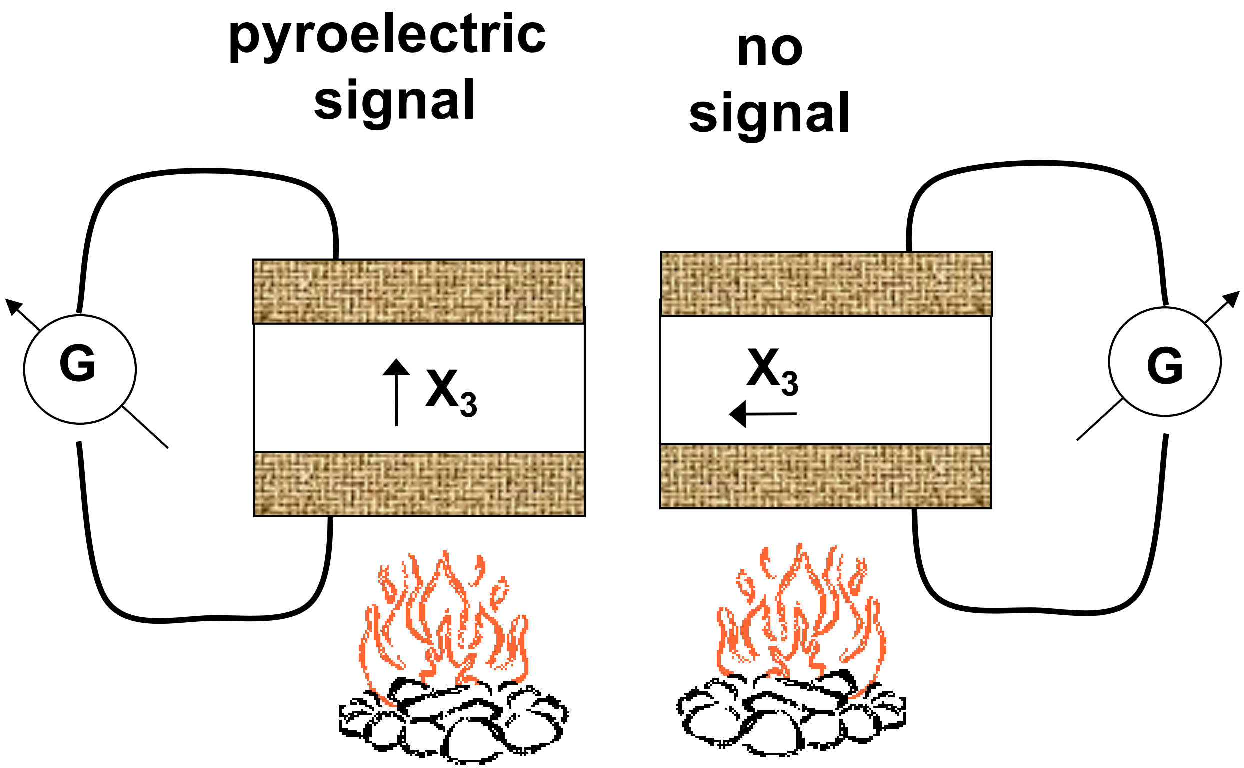
Anisotropy of pyroelectric effect

$4mm$



$A = Pb$

$B = Ti$



Applications: pyroelectric sensors

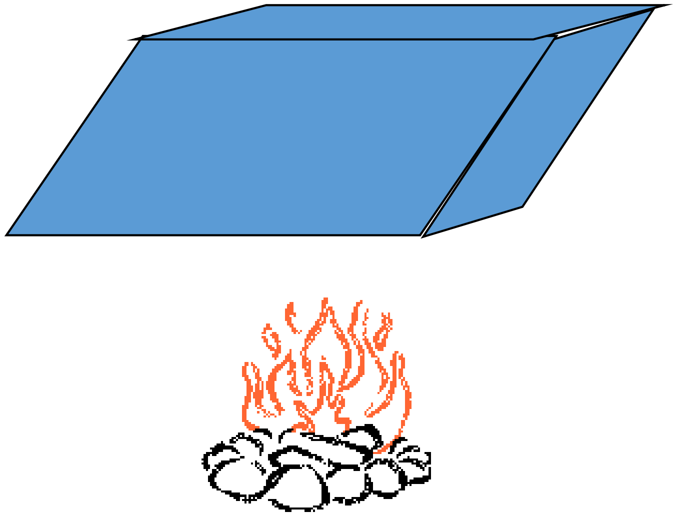
• Sensors for motion, gas, food, or flame

• mK –sensitivity (in principle even μK-range), human presence up to 20-30 m

• gas sensors: IR-emitters, IR pass through the gas sample, then detecting if a certain IR wavelength is received on the other side.
If it is not received, the gas that absorbs that wavelength must be present in the sample – e.g. CO and CO_2

• flame sensors, food sensors, IR imaging
(**Different food materials absorb and reflect infrared light in unique ways, depending on their composition (e.g., moisture, fat, proteins, and carbohydrates)**

Thermal expansion



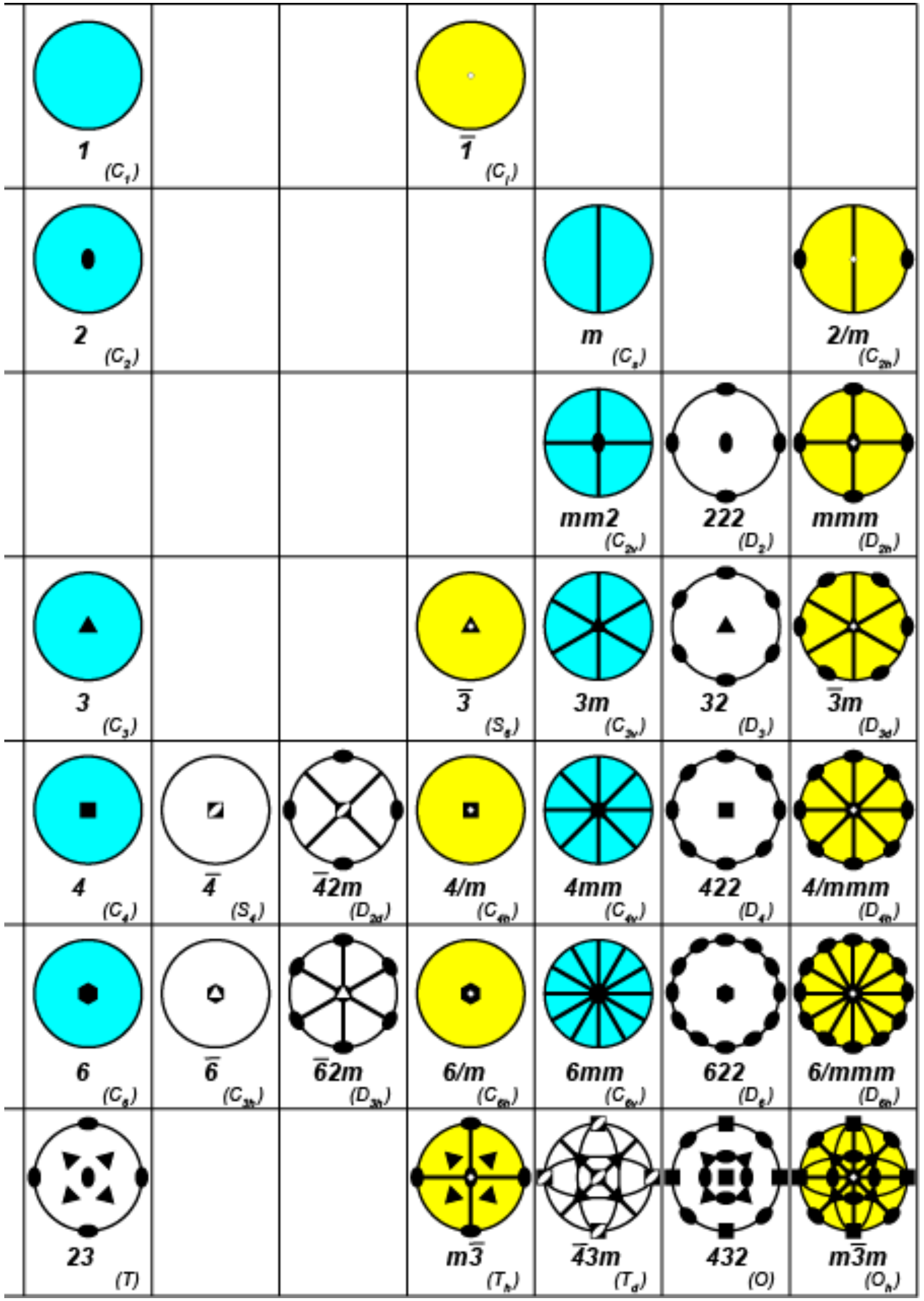
$$\delta T \Rightarrow \varepsilon_{ij}$$ **Strain**

$$\varepsilon_{ij} = \alpha_{ij} \delta T$$

α_{ij} **Tensor of coefficients of thermal expansion**

Symmetric second rank tensor like $K_{ij} = K_{ji}$

Effect of Neumann in conventional axes



$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ & \alpha_{22} & \alpha_{23} \\ & & \alpha_{33} \end{pmatrix}$$

$$\begin{pmatrix} \alpha_{11} & 0 & \alpha_{13} \\ & \alpha_{22} & 0 \\ & & \alpha_{33} \end{pmatrix}$$

$$\begin{pmatrix} \alpha_{11} & 0 & 0 \\ & \alpha_{22} & 0 \\ & & \alpha_{33} \end{pmatrix}$$

$$\begin{pmatrix} \alpha_{1} & 0 & 0 \\ & \alpha_{1} & 0 \\ & & \alpha_{3} \end{pmatrix}$$

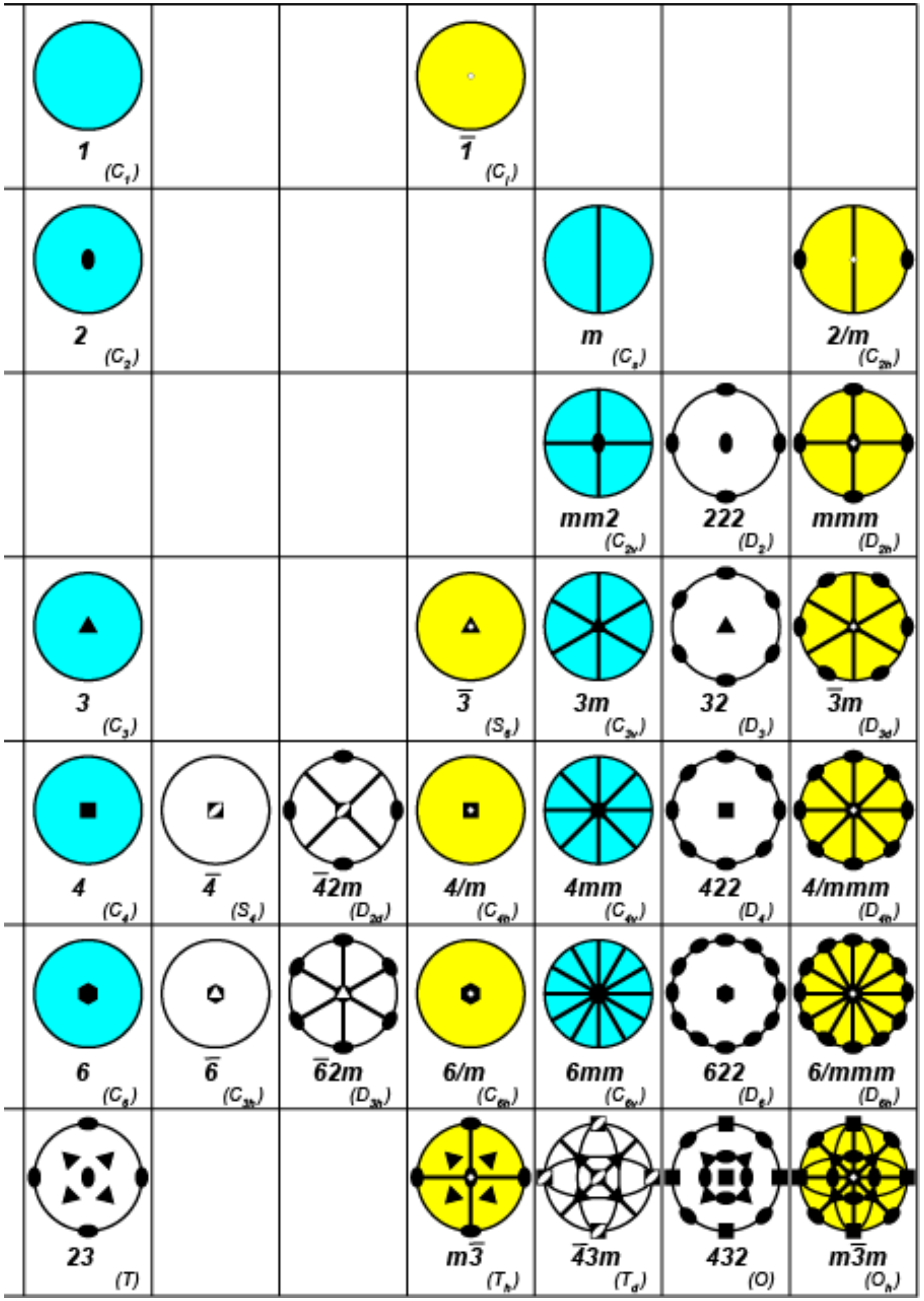
$\infty \quad \infty m \quad \infty 2$

$\infty / m \quad \infty / mm$

$$\begin{pmatrix} \alpha & 0 & 0 \\ & \alpha & 0 \\ & & \alpha \end{pmatrix}$$

$\infty\infty \quad \infty\infty m$

Symmetry of thermal expansion



mmm

$$\begin{pmatrix} \alpha_{11} & 0 & 0 \\ & \alpha_{22} & 0 \\ & & \alpha_{33} \end{pmatrix}$$

∞ $\quad$ ∞m

$\infty 2$ $\quad$ ∞ / m

∞ / mm

∞ / mm

$$\begin{pmatrix} \alpha_1 & 0 & 0 \\ & \alpha_1 & 0 \\ & & \alpha_3 \end{pmatrix}$$

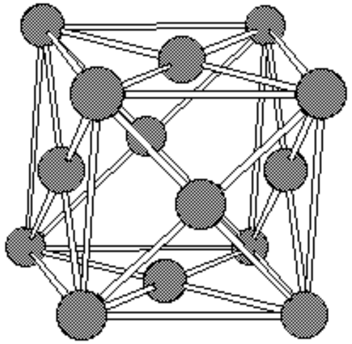
$\infty\infty m$ $\quad$ $\infty\infty$

$$\begin{pmatrix} \alpha & 0 & 0 \\ & \alpha & 0 \\ & & \alpha \end{pmatrix}$$

$\infty\infty m$

Thermal expansion: examples

Cu

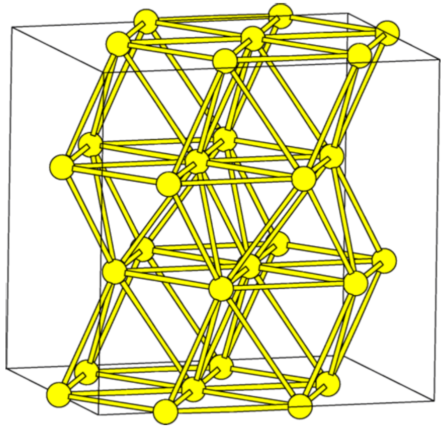


$$m\bar{3}m$$

$$\begin{pmatrix} \alpha & 0 & 0 \\ & \alpha & 0 \\ & & \alpha \end{pmatrix}$$

$$\alpha = 16 \times 10^{-6}\ \mathrm{K}^{-1}$$

Zn



$$6/mmm$$

$$\begin{pmatrix} \alpha_1 & 0 & 0 \\ & \alpha_1 & 0 \\ & & \alpha_3 \end{pmatrix}$$

	α_1	α_3
60 K	−2	55
150 K	8	65
300 K	13	64

$\times 10^{-6}\ \mathrm{K}^{-1}$

Constitutive equations of linear electro-thermo-mechanical response

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in}\sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm}\sigma_m + \alpha_n \delta T$$

Heat per unit volume

$$\delta M = \cdot\, C\delta T$$

Heat capacity

Constitutive equations of linear electro-thermo-mechanical response

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in}\sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm}\sigma_m + \alpha_n \delta T$$

$$\delta M = A_i E_i + B_m \sigma_m + C\delta T$$

1st rank

2nd rank

Electrocaloric effect

Piezocaloric effect

Constitutive equations of linear electro-thermo-mechanical response

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in}\sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm}\sigma_m + \alpha_n \delta T$$

$$\delta M = A_i E_i + B_m \sigma_m + C\delta T$$

$$A_i = T p_i \qquad B_m = T\alpha_m$$

Constitutive equations of linear electro-thermo-mechanical response

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in}\sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm}\sigma_m + \alpha_n \delta T$$

$$\delta S = \frac{\delta M}{T} = p_i E_i + \alpha_m \sigma_m + \frac{C}{T}\delta T$$

Entropy per unit volume

Remarkable symmetry of the constitutive equations

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in}\sigma_n + p_i \delta T$$

$$\varepsilon_n = d_{in} E_i + s_{nm}\sigma_m + \alpha_n \delta T$$

$$\delta S = p_i E_i + \alpha_m \sigma_m + \frac{C}{T}\delta T$$

The reason?

All these remarkable experimental findings
can be explained
taking into account
the energy aspect of the problem

Thermodynamics

Energy

$$\Delta U = A$$

Energy conservation law

Work

Internal energy

Heat

$$\Delta U_{\text{int}} = A + m$$

1st law of thermodynamics

Work

Thermodynamics

Entropy

$$\boxed{m = T \cdot \Delta s}$$

2nd law of thermodynamics (at the equilibrium)

$$\boxed{m = V \cdot T \cdot \Delta S}$$

$\boxed{S}$ **Entropy density**

Thermodynamics

$$\Delta U_{\text{int}} = V\int\left(E_i dD_i + \sigma_n d\varepsilon_n\right) + V \cdot T \cdot \Delta S$$

Work **Heat**

$$\boxed{W_{\text{int}} = U_{\text{int}} / V}$$

Internal energy density

$$\boxed{dW_{\text{int}} = E_i dD_i + \sigma_n d\varepsilon_n + TdS}$$

Legendre transformation

$$dW_{\text{int}} = E_i dD_i + \sigma_n d\varepsilon_n + TdS$$

$$G = W_{\text{int}} - E_i D_i - \sigma_n \varepsilon_n - TS$$

$$dG = -D_i dE_i - \varepsilon_n d\sigma_n - SdT$$

$$D_i = -\left(\frac{\partial G}{\partial E_i}\right)_{T,\sigma} \qquad \varepsilon_n = -\left(\frac{\partial G}{\partial \sigma_n}\right)_{T,E} \qquad S = -\left(\frac{\partial G}{\partial T}\right)_{E,\sigma}$$

Pyroelectric vs. elecrocaloric effects

pyroelectric effect

$$D_i = p_i \delta T$$

$$p_i = \left(\frac{\partial D_i}{\partial T}\right)_{\sigma,E}$$

$$D_i = -\left(\frac{\partial G}{\partial E_i}\right)_{T,\sigma}$$

Electrocaloric effect

$$\delta M = A_i E_i$$

$$\delta M = T\delta S$$

$$A_i = T\left(\frac{\partial S}{\partial E}\right)_{\sigma,T}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{E,\sigma}$$

$$p_i = -\frac{\partial^2 G}{\partial T \partial E_i} \Rightarrow \boxed{A_i = T p_i} \Leftarrow A_i = -T\frac{\partial^2 G}{\partial E_i \partial T}$$

Electrocaloric effect

$$\delta S = p_i E_i + \alpha_n \sigma_n + \frac{C}{T} \delta T$$

Under adiabatic conditions (thermal insulation)

δS = 0

and mechanically free $\sigma_n = 0$

$$\delta T = -\frac{T}{C} p_i E_i$$

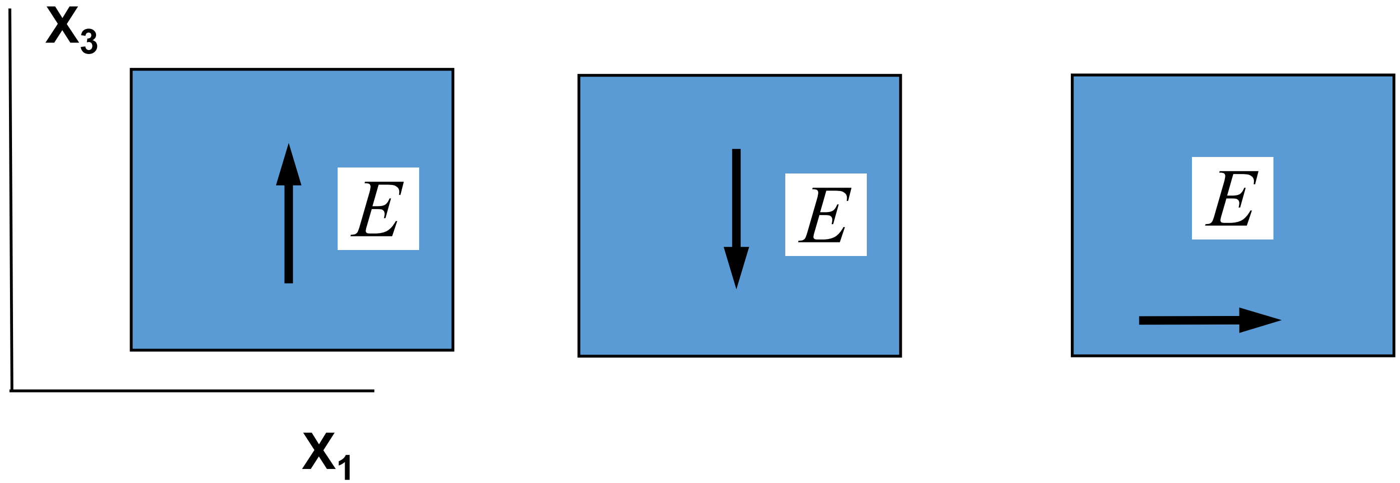
Anisotropy of electrocaloric effect

$$\delta T = -\frac{T}{C} p_i E_i$$

$4mm$

$PbTiO_3$

$$\begin{pmatrix} 0 \\ 0 \\ p \end{pmatrix}$$



$$\frac{\delta T}{T} = -\frac{pE}{C}$$

$$\frac{\delta T}{T} = \frac{pE}{C}$$

$$\delta T = 0$$

Electrocaloric effect. Example

$$\delta T = -\frac{T}{C} p_i E_i$$

$4mm$

$PbTiO_3$

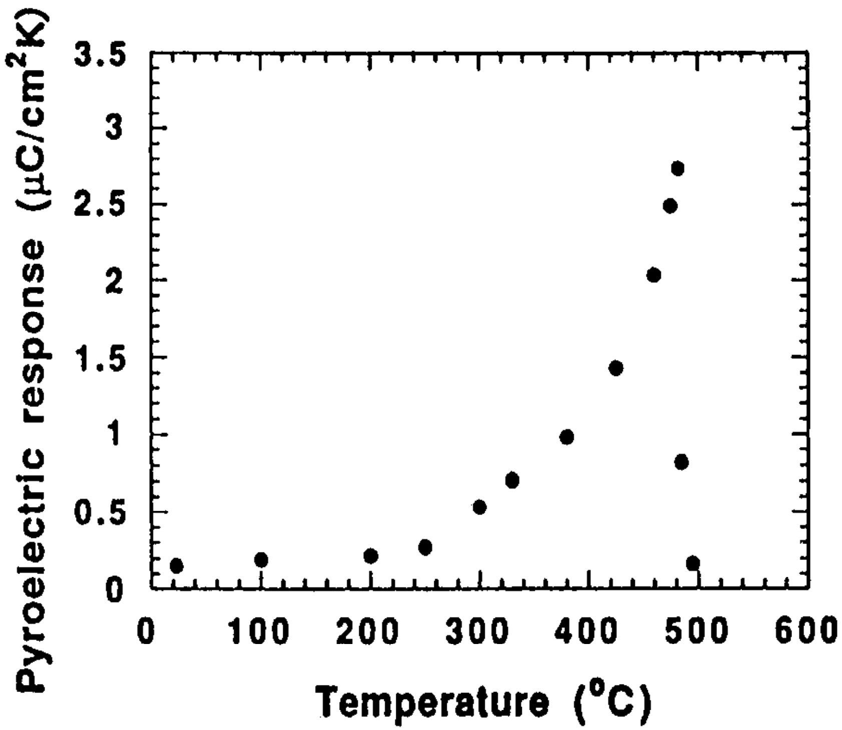
$$\begin{pmatrix} 0 \\ 0 \\ p \end{pmatrix}$$

$$p = 0.02 \text{ C/m}^2\text{K}$$

$$E = 1 \text{ kV/cm} = 10^5 \text{ V/m}$$

$$C \approx 3.5 \times 10^6 \text{ J/m}^3\text{K}$$

$$\frac{\delta T}{T} = \frac{pE}{C} \cong 10^{-3}$$



For long time was considered as a weak effect…

Giant electrocaloric effect

Science

Giant Electrocaloric Effect in Thin-Film $PbZr_{0.95}Ti_{0.05}O_3$

A. S. Mischenko,[1*] Q. Zhang,[2] J. F. Scott,[3] R. W. Whatmore,[2] N. D. Mathur[1]

An applied electric field can reversibly change the temperature of an electrocaloric material under adiabatic conditions, and the effect is strongest near phase transitions. We demonstrate a giant electrocaloric effect (0.48 kelvin per volt) in 350-nanometer $PbZr_{0.95}Ti_{0.05}O_3$ films near the ferroelectric Curie temperature of 222°C. A large electrocaloric effect may find application in electrical refrigeration.

Science **311** (5765), 1270-1271.
DOI: 10.1126/science.1123811

Giant Electrocaloric Effect in Thin-Film $PbZr_{0.95}Ti_{0.05}O_3$

A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore and N. D. Mathur

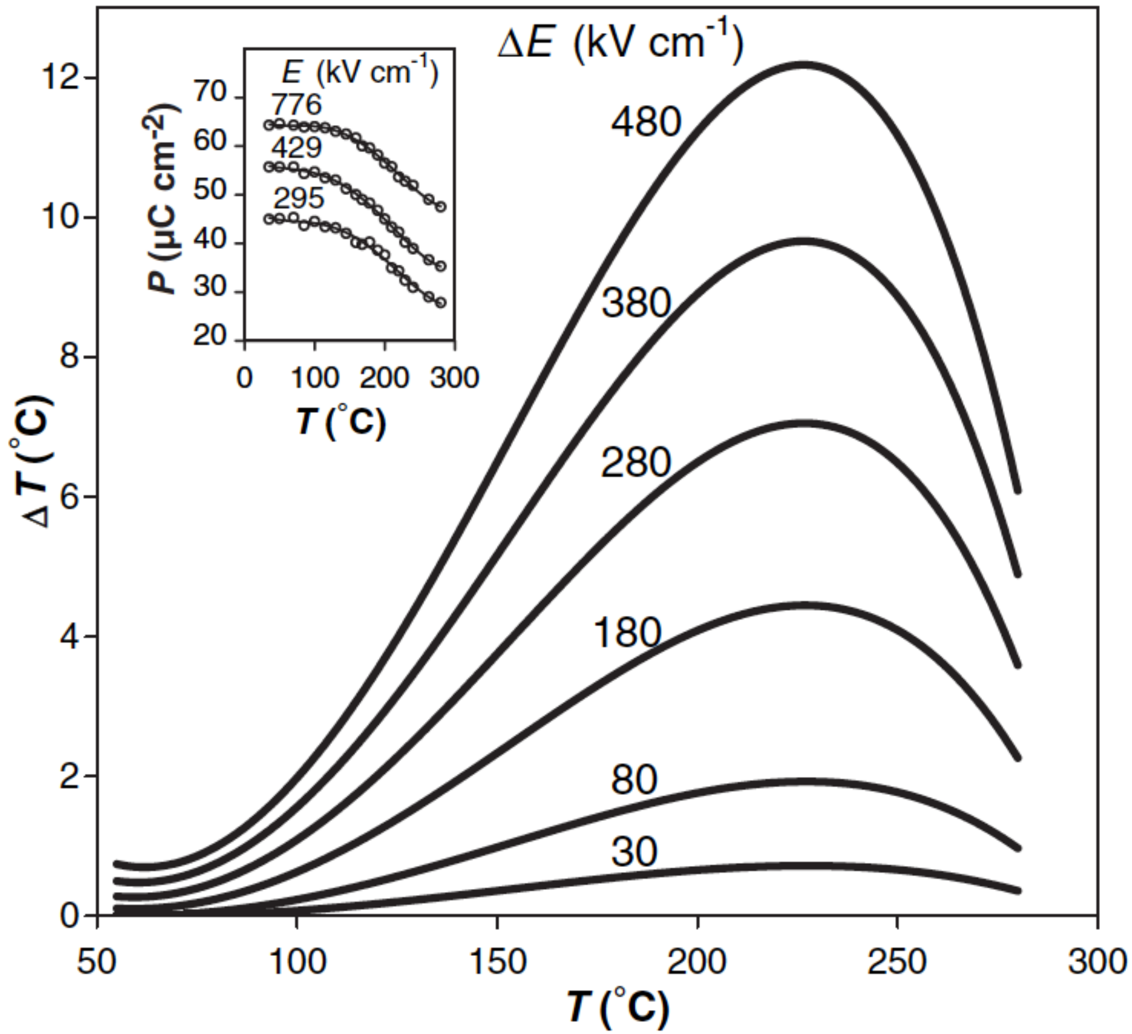


Fig. 2. Electrocaloric temperature changes ΔT due to applied ΔE. Calculations were performed using Eq. 1 with selected values of $\Delta E = E_2 - E_1$, where $E_2 = 776$ kV cm^{-1}. The peak value of $\Delta T = 12$ K occurs in $\Delta E = 480$ kV cm^{-1} at $T_{EC} = 226°C$, where $|\partial P/\partial T|$ is maximized. (**Inset**) $P(T)$ at selected applied fields E. The lines represent fourth-order polynomial fits to data extracted from the upper branches of 19 hysteresis loops in $E > 0$. Four of the 19 loops are shown in Fig. 1, A to D.

Linear electro-thermo-mechanical response under different conditions

Adiabatic ←→ Isothermal

Clamped ← → Mechanically free

Short-circuit ←→ Open-circuit

Dielectric constant

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in} \sigma_n + p_i \delta T$$

dielectric constant measured
in mechanically free
crystal
at isothermal conditions

1. Non-piezoelectric – permittivity is independent of measurements conditions.

2.Piezoelectric/non-polar - permittivity is dependent on mechanical measurement conditions.

3.Polar - permittivity is dependent on both mechanical and thermal measurement conditions.

Adiabatic dielectric constant in a mechanically free sample

$$D_i = \varepsilon_0 K_{ij} E_j + p_i \delta T$$

$$\delta S = p_i E_i + \frac{C}{T} \delta T$$

$$\delta S = 0$$

$$\sigma_n = 0$$

$$\delta T = -\frac{T}{C} p_i E_i \Rightarrow D_i = \varepsilon_0 K_{ij} E_j - \frac{T}{C} p_i p_j E_j$$

$$K_{ij}^{ad} = K_{ij} - \frac{T}{\varepsilon_0 C} p_i p_j$$

Elastic compliance

$$\varepsilon_n = d_{in}E_i + s_{nm}\sigma_m + \alpha_n \delta T$$

Elastic compliance measured in a short-circuited crystal at isothermal conditions

1. Non-piezoelectrics - compliance is independent of the electrical conditions but sensitive to thermal conditions

2. Piezoelectrics - compliance is sensitive to both electrical and thermal conditions

Other effects sensitive to conditions of measurements

$$D_i = \varepsilon_0 K_{ij} E_j + d_{in}\sigma_n + \boxed{p_i \delta T}$$

$$\varepsilon_n = d_{in} E_i + s_{nm}\sigma_m + \boxed{\alpha_n \delta T}$$

$$\delta S = p_i E_i + \alpha_m \sigma_m + \boxed{\frac{C}{T}\delta T}$$

1.”Clamped” and “free” pyroelectricity

2. Short- and open-circuit thermal expansion

3. Heat capacity (short- /open-circuit and clamped/free mechanically)

Linear electro-thermo-mechanical response under different conditions

Adiabatic ←→ Isothermal

Clamped ← → Mechanically free

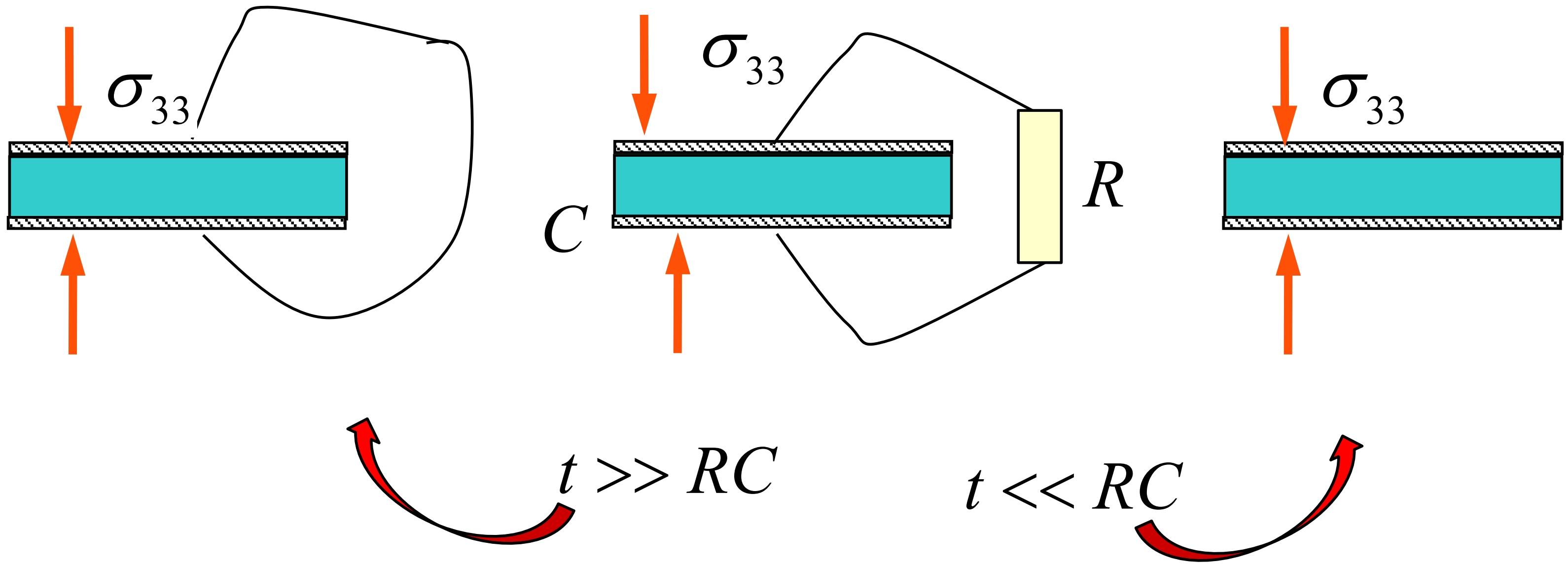
Short-circuit ←→ Open-circuit

These cases may not discuss the dynamic situation

Linear electro-thermo-mechanical response under different conditions

Young modulus

Short-circuit ← mixed → Open-circuit



Essential

1. Electrical, mechanical, and thermal effects in solids are linked. The question if any two effects are linked can be solved using the symmetry and thermodynamic arguments.

2.The response of a solid to electrical, mechanical, and thermal perturbations can be sensitive to the conditions of the experiment.

3. Electrical conditions range between “open-circuit” and “short-circuit”.

4. Mechanical conditions range between “free” and “clamped”.

5. Thermal conditions range between “isothermal” and “adiabatic”.