Oxide multicalorics

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Oxide multicalorics

Background

Brief history of calorics

Thermodynamics and measurements

Multicaloric $BaTiO_3$

Multicaloric $(NH_4)_2SO_4$

Colossal barocaloric plastic crystals

Cooling

Vapour-based refrigeration

Advantages:

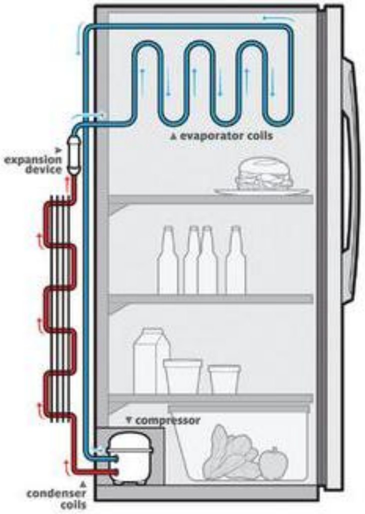
Established technology
(cheap, reliable)

Disadvantages:

Harmful fluids
40-60% energy efficient
Noisy
Not suitable for miniaturization or fast start-up

Cooling

Vapour-based refrigeration



Advantages:

Established technology
(cheap, reliable)

Disadvantages:

Harmful fluids
40-60% energy efficient
Noisy
Not suitable for miniaturization or fast start-up

Alternatives: solid-state refrigeration

Thermoelectric (~ 10%)
Thermionic (~ 80% but very high *T*)
Laser cooling (~ 2%)

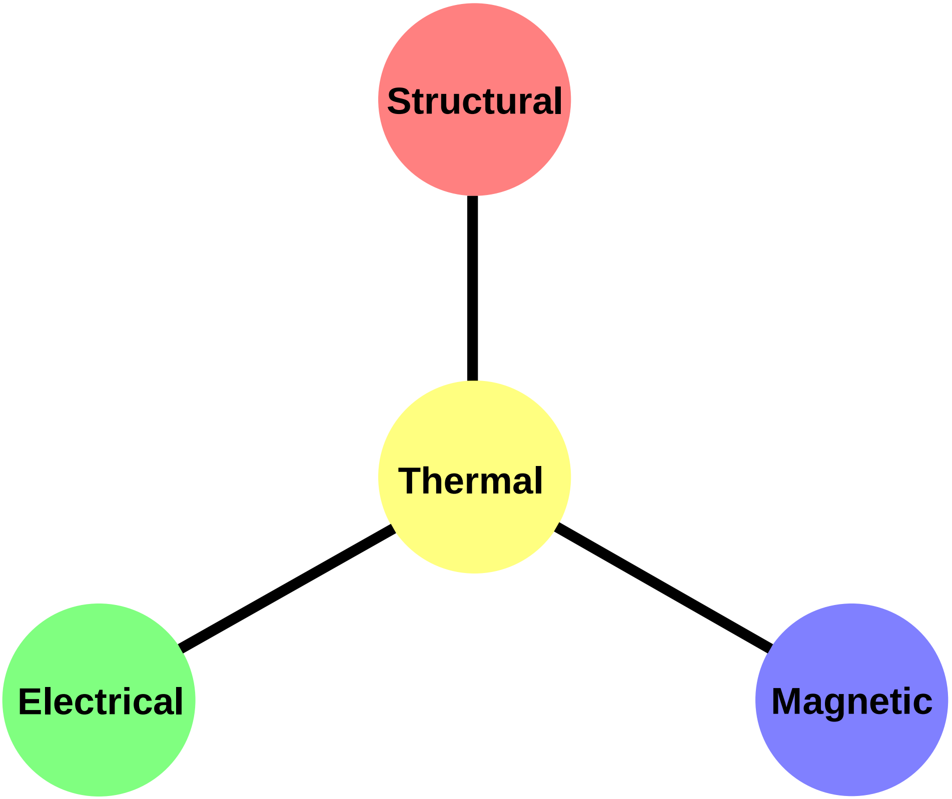
Caloric effects

Coupling between ferroic and thermal properties

Magnetocaloric (MC) effect

Electrocaloric (EC) effect

Mechanocaloric (mC) effect
elastocaloric (eC) effect
barocaloric (BC) effect



Large near phase transitions

Caloric effects

Coupling between ferroic and thermal properties

Magnetocaloric (MC) effect

Electrocaloric (EC) effect

Mechanocaloric (mC) effect
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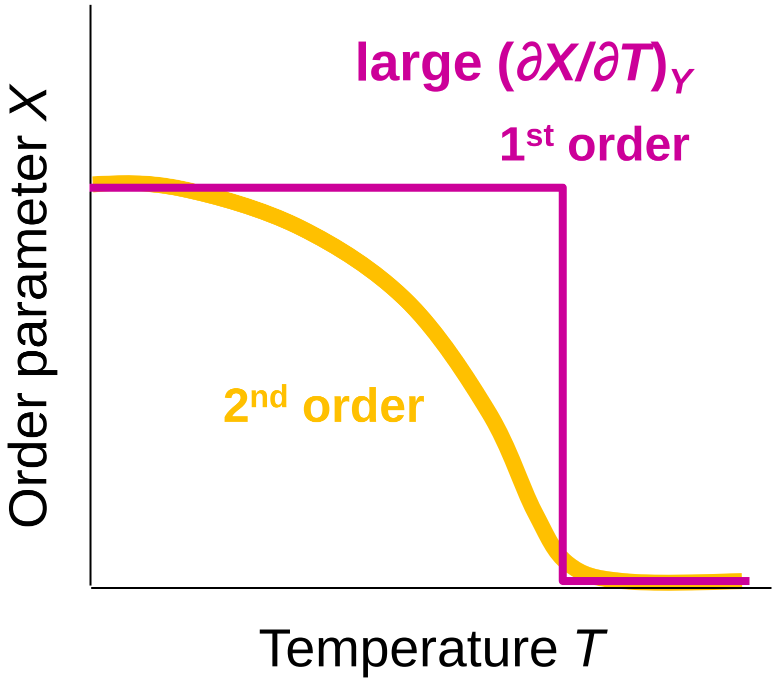
barocaloric (BC) effect



Largest near 1st phase transitions

Caloric effects

Coupling between ferroic and thermal properties

Magnetocaloric (MC) effect

Electrocaloric (EC) effect

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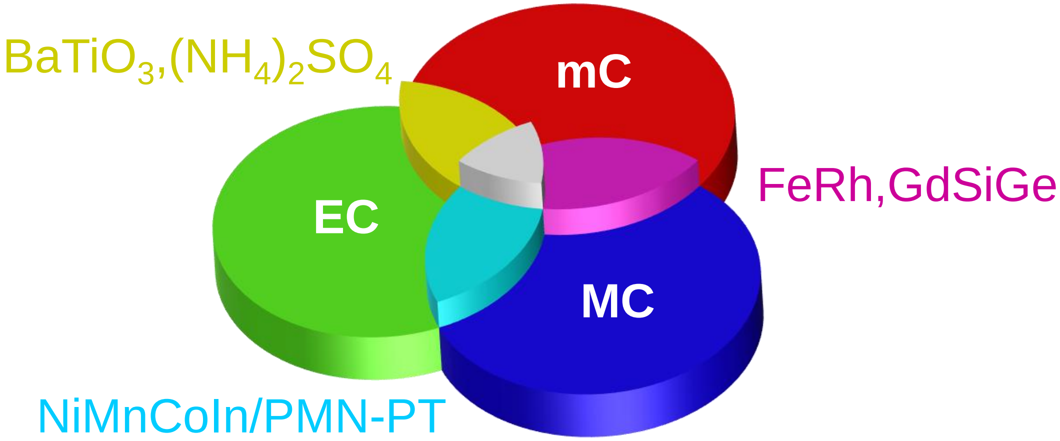
elastocaloric (eC) effect
barocaloric (BC) effect

MULTICALORICS



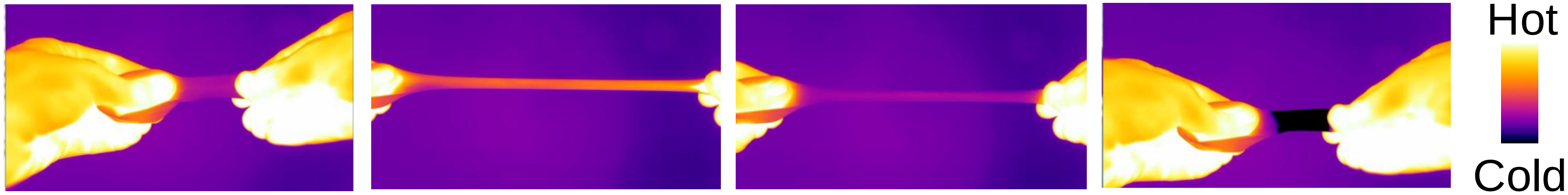
$BaTiO_3$,$(NH_4)_2SO_4$

FeRh,GdSiGe

NiMnCoIn/PMN-PT

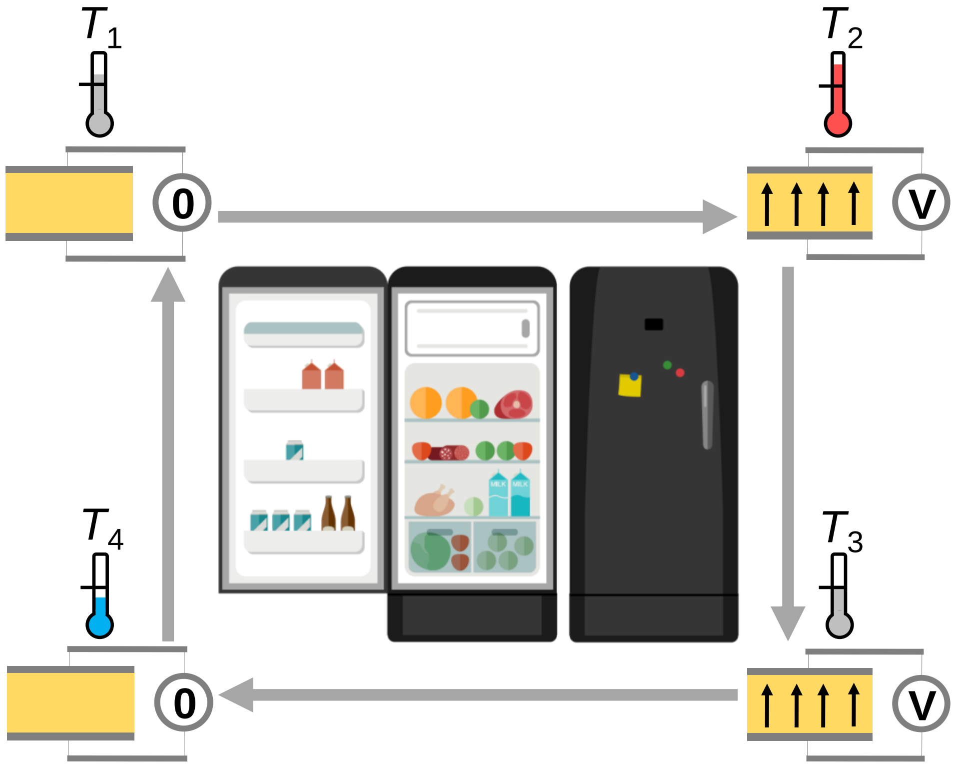
Stern-Taulats *et al.* MRS Bulletin **43**, 295 (2018)

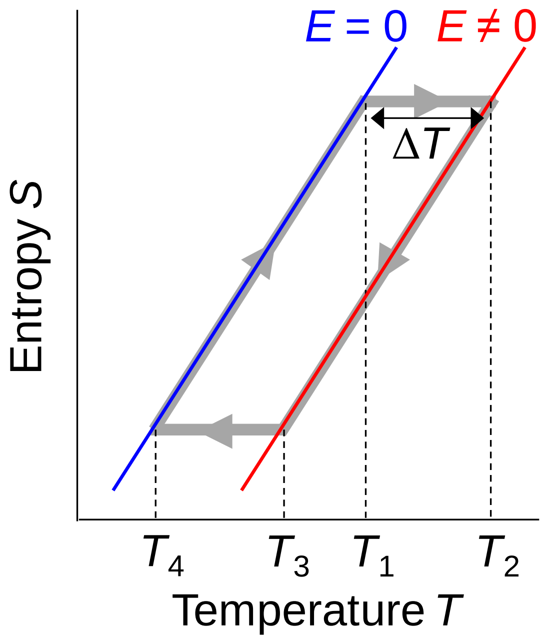
Caloric effects



Proposed for cooling applications

e.g. Electrocaloric effect

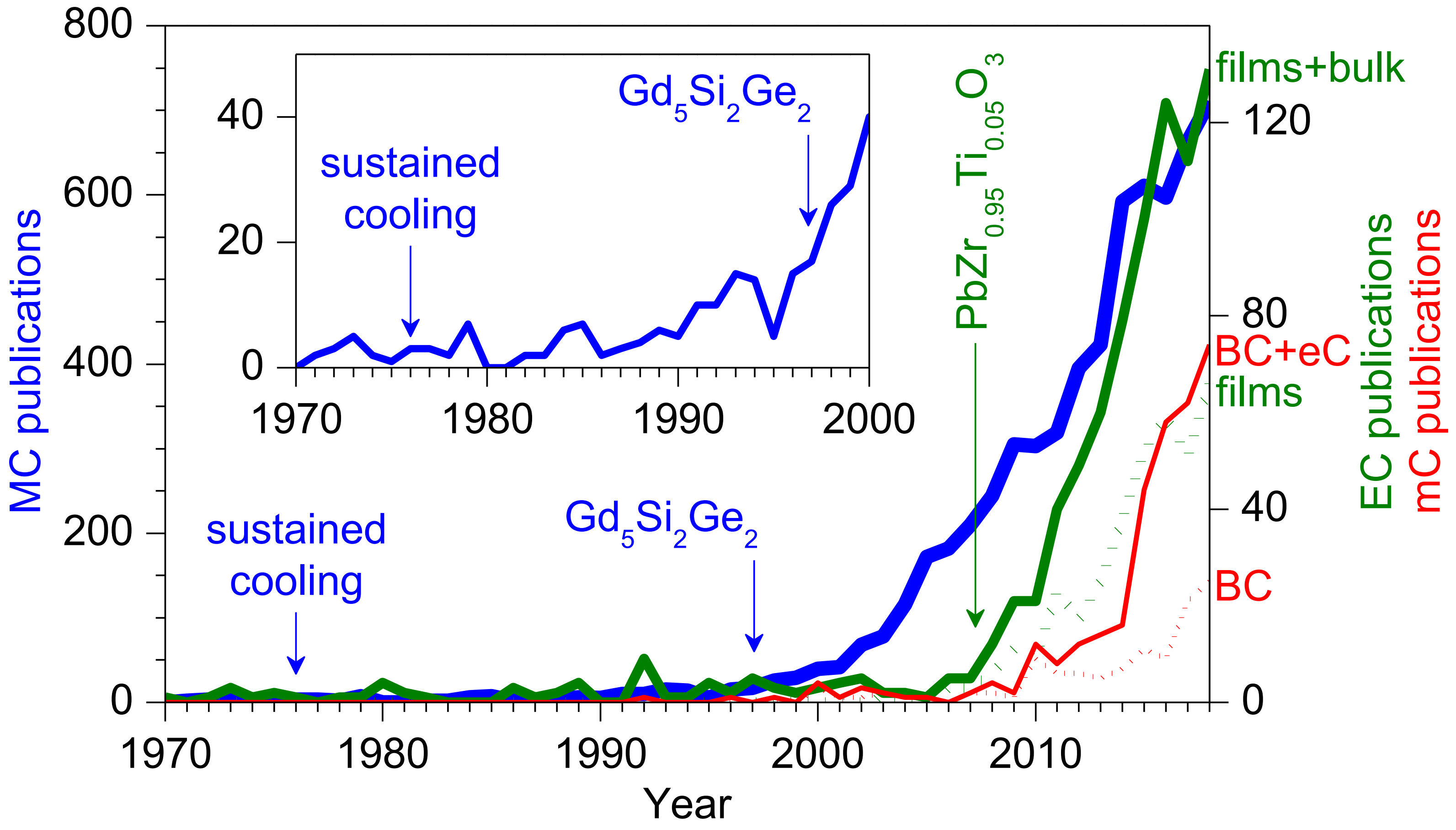




Moya *et al.* MRS Bulletin **43**, 291 (2018)

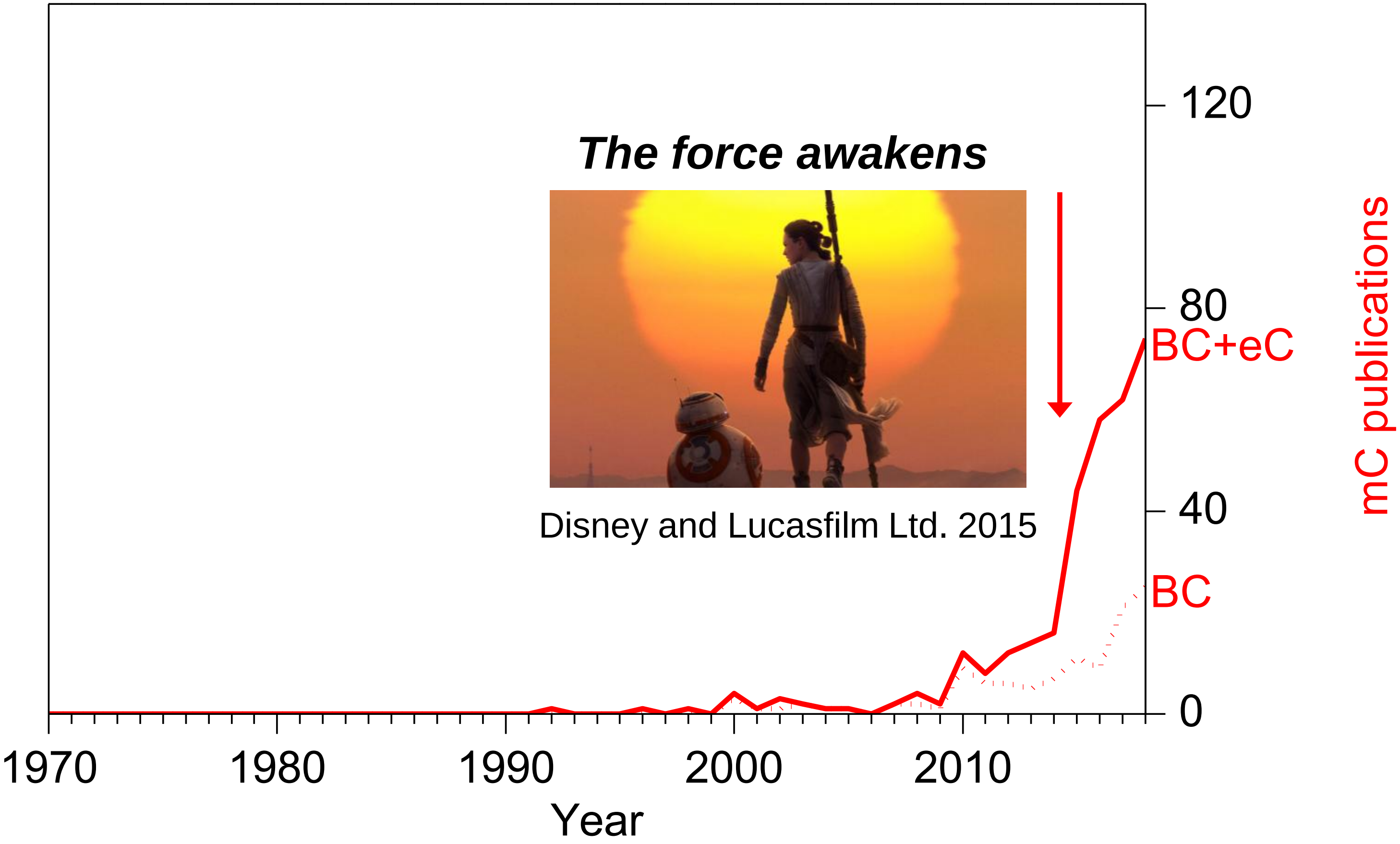
Useful for solid-state cooling
(environmentally friendly)

Caloric research



updated from Moya *et al.*, *Nature Materials* **13**, 439 (2014)

Caloric research



The force awakens

Disney and Lucasfilm Ltd. 2015

updated from Moya *et al.*, *Nature Materials* **13**, 439 (2014)

Review Articles
Magnetocalorics & Electrocalorics & Mechanocalorics

nature materials

REVIEW ARTICLE

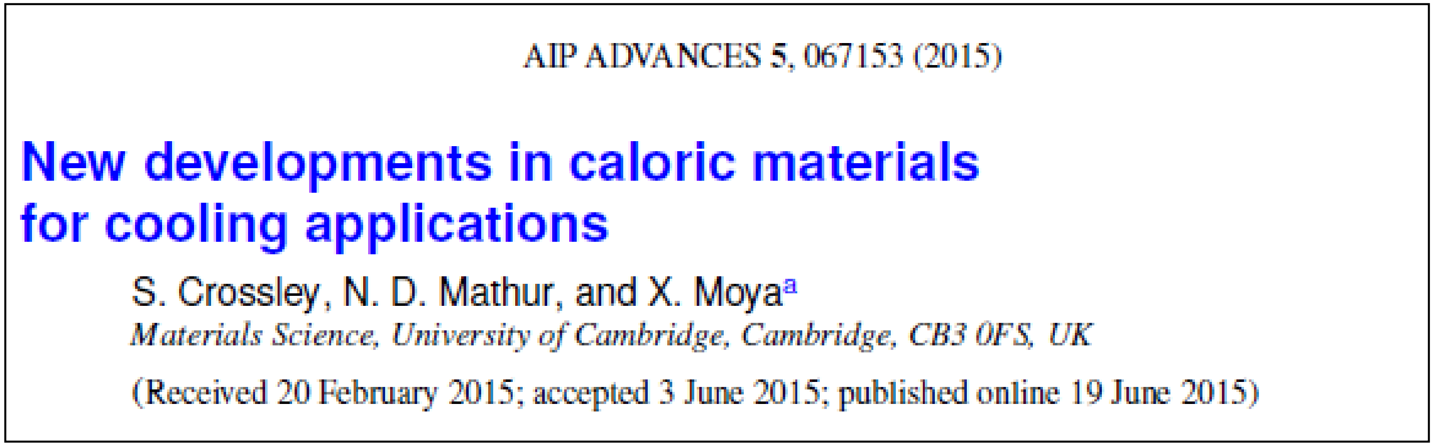
PUBLISHED ONLINE: 22 APRIL 2014 | DOI: 10.1038/NMAT3951

Caloric materials near ferroic phase transitions

X. Moya[1,2], S. Kar-Narayan[1] and N. D. Mathur[1]*

A magnetically, electrically or mechanically responsive material can undergo significant thermal changes near a ferroic phase transition when its order parameter is modified by the conjugate applied field. The resulting magnetocaloric, electrocaloric and mechanocaloric (elastocaloric or barocaloric) effects are compared here in terms of history, experimental method, performance and prospective cooling applications.

Nature Materials **13**, 439 (2014)



AIP ADVANCES 5, 067153 (2015)

New developments in caloric materials for cooling applications

S. Crossley, N. D. Mathur, and X. Moya[a]
Materials Science, University of Cambridge, Cambridge, CB3 0FS, UK

(Received 20 February 2015; accepted 3 June 2015; published online 19 June 2015)

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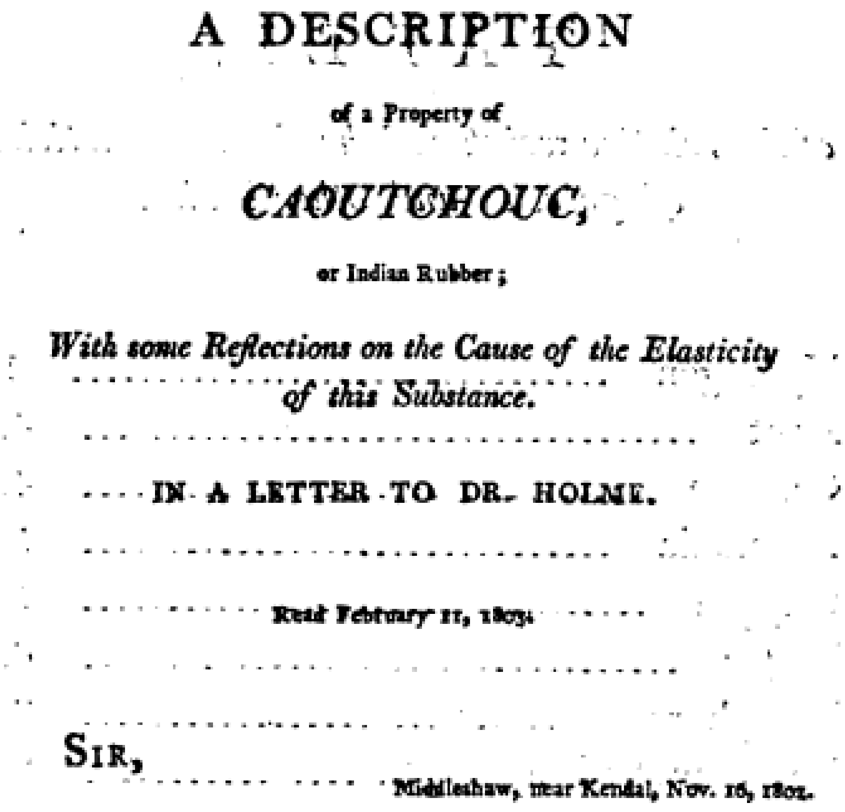
Multicaloric $(NH_4)_2SO_4$

Colossal barocaloric plastic crystals

First observation: eC effects in rubber

Qualitative study: ΔT detected using lips



A DESCRIPTION

of a Property of

CAOUTCHOUC,

or Indian Rubber;

With some Reflections on the Cause of the Elasticity of this Substance.

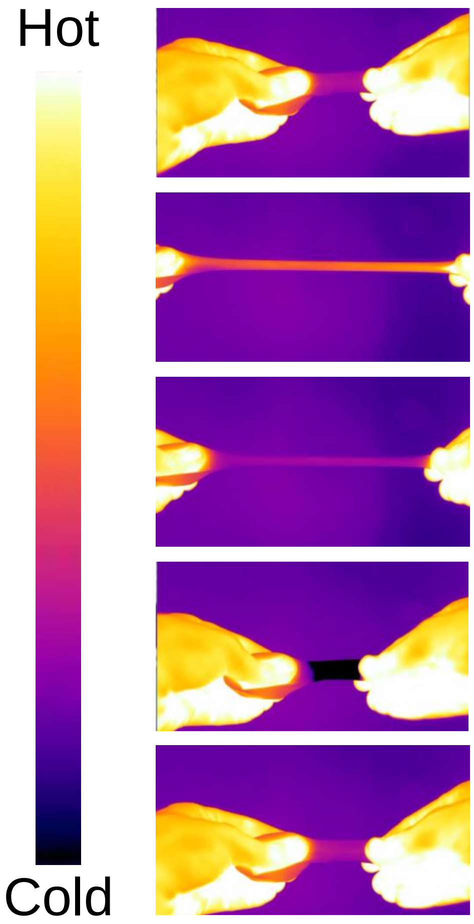
IN A LETTER TO DR. HOLME.

Read February 11, 1803.

SIR,

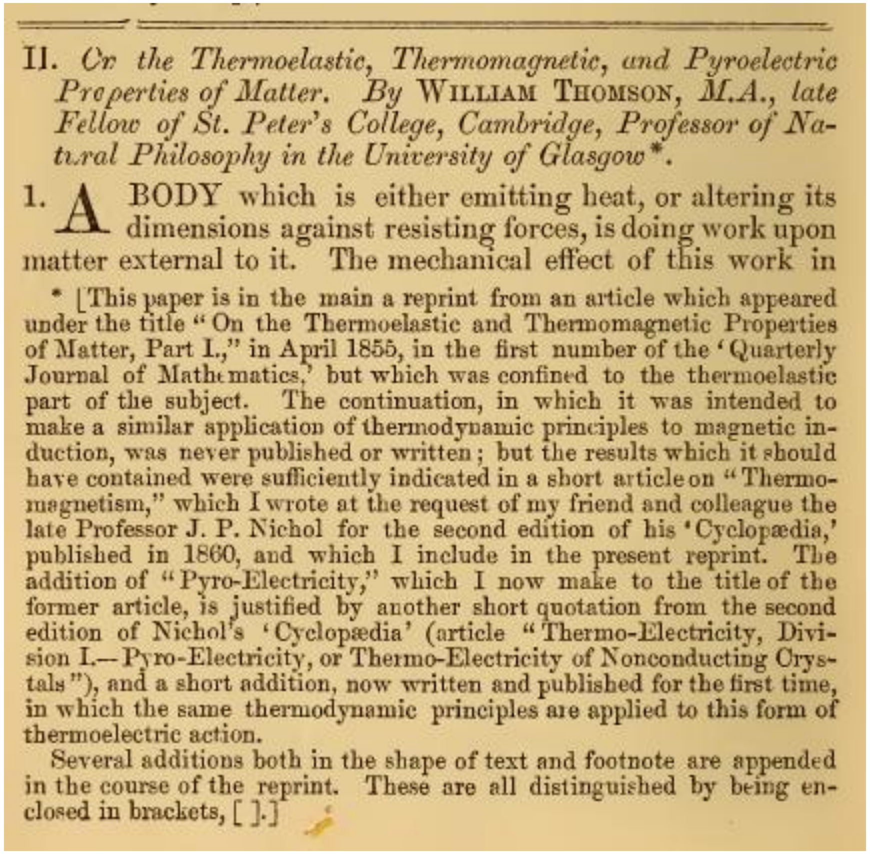
Middleshaw, near Kendal, Nov. 16, 1802.

Gough, *Mem. Lit. Phil. Soc. Manchester* **1**, 288 (1805)



Thermodynamic interpretation

First for eC effects in 1855, later extended to MC and EC



II. *On the Thermoelastic, Thermomagnetic, and Pyroelectric Properties of Matter.* *By* William Thomson, *M.A., late Fellow of St. Peter's College, Cambridge, Professor of Natural Philosophy in the University of Glasgow**.

1. A BODY which is either emitting heat, or altering its dimensions against resisting forces, is doing work upon matter external to it. The mechanical effect of this work in

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* [This paper is in the main a reprint from an article which appeared under the title "On the Thermoelastic and Thermomagnetic Properties of Matter, Part I.," in April 1855, in the first number of the 'Quarterly Journal of Mathematics,' but which was confined to the thermoelastic part of the subject. The continuation, in which it was intended to make a similar application of thermodynamic principles to magnetic induction, was never published or written; but the results which it should have contained were sufficiently indicated in a short article on "Thermomagnetism," which I wrote at the request of my friend and colleague the late Professor J. P. Nichol for the second edition of his 'Cyclopædia,' published in 1860, and which I include in the present reprint. The addition of "Pyro-Electricity," which I now make to the title of the former article, is justified by another short quotation from the second edition of Nichol's 'Cyclopædia' (article "Thermo-Electricity, Division I.—Pyro-Electricity, or Thermo-Electricity of Nonconducting Crystals"), and a short addition, now written and published for the first time, in which the same thermodynamic principles are applied to this form of thermoelectric action.

Several additions both in the shape of text and footnote are appended in the course of the reprint. These are all distinguished by being enclosed in brackets, [ ].]

Maxwell relations:

$$\Delta S = \int_0^Y \left(\frac{\partial X}{\partial T}\right)_{Y'} dY'$$

$$Q = T\Delta S$$

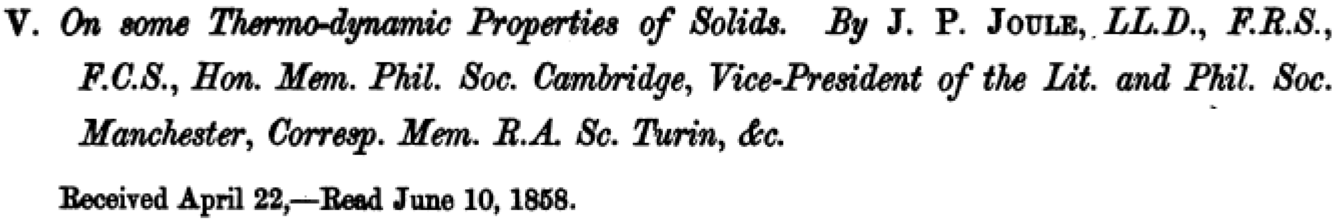
$$\Delta T = -\frac{T}{C}\Delta S$$

$X = M, P, -V \quad Y = \mu_0 H, E, p$

Thomson, *Lond. Edinb. Dublin Phil. Mag. J. Sci.* **5,** 4 (1878)

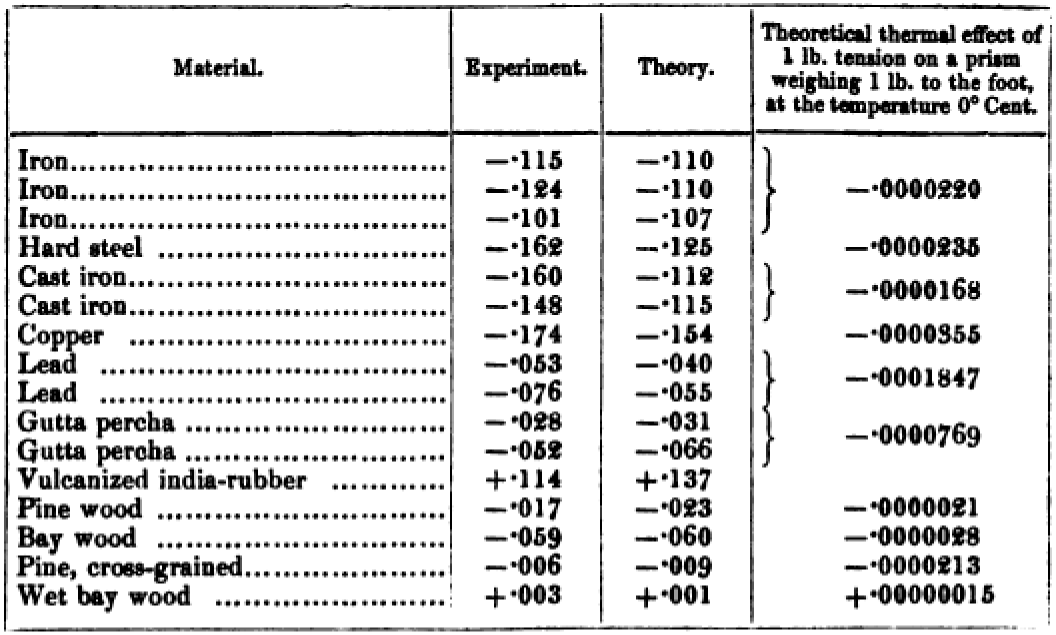
First quantitative eC study

Number of materials studied, away from phase transitions



V. *On some Thermo-dynamic Properties of Solids. By* J. P. Joule, *LL.D., F.R.S., F.C.S., Hon. Mem. Phil. Soc. Cambridge, Vice-President of the Lit. and Phil. Soc. Manchester, Corresp. Mem. R.A. Sc. Turin, &c.*

Received April 22,—Read June 10, 1858.



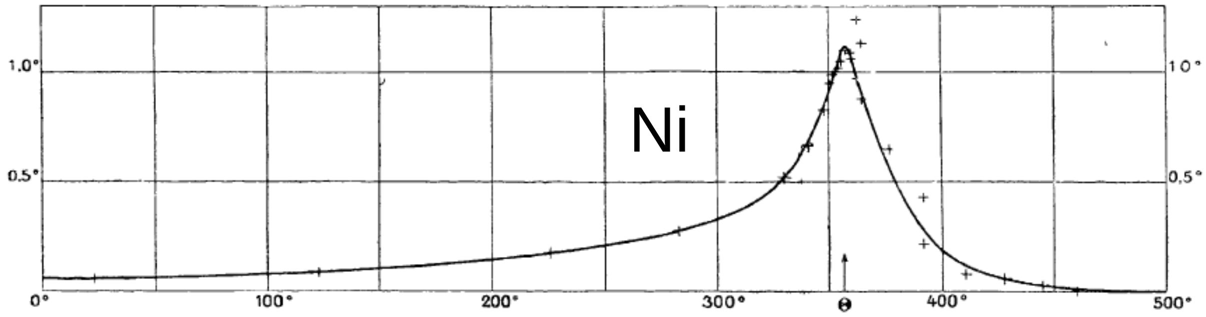
Material.	Experiment.	Theory.	Theoretical thermal effect of 1 lb. tension on a prism weighing 1 lb. to the foot, at the temperature 0° Cent.
Iron	—·115	—·110	—·0000220
Iron	—·124	—·110	
Iron	—·101	—·107	
Hard steel	—·162	—·125	—·0000235
Cast iron	—·160	—·112	—·0000168
Cast iron	—·148	—·115	
Copper	—·174	—·154	—·0000355
Lead	—·053	—·040	—·0001847
Lead	—·076	—·055	
Gutta percha	—·028	—·031	—·0000769
Gutta percha	—·052	—·066	
Vulcanized india-rubber	+·114	+·137	
Pine wood	—·017	—·023	—·0000021
Bay wood	—·059	—·060	—·0000028
Pine, cross-grained	—·006	—·009	—·0000213
Wet bay wood	+·003	+·001	+·00000015

Joule, *Phil. Trans.* **149,** 91-131 (1859)

Caloric effects near phase transitions

First studies, small MC and EC effects near 2nd order transitions

Weiss and Piccard
J. Phys. Theor. Appl. **7,** 103-109
(1917)

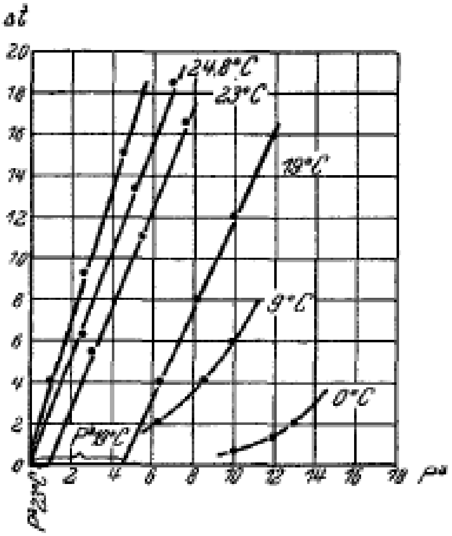


Ni

(not Warburg in 1881…)

Kobeko and Kurtschatov
Z. Phys. **66,** 192-205 (1930)

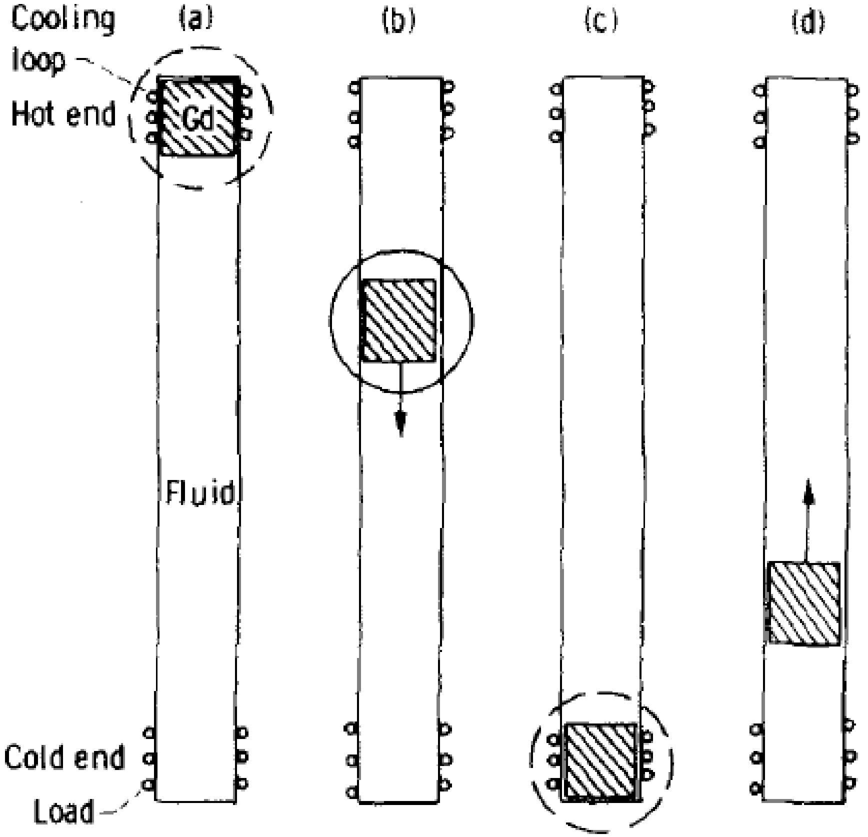
(qualitative study)



$NaKC_4H_4O_6 \cdot 4H_2O$

First MC room-temperature refrigerator prototype

Use of regenerator increases temperature span



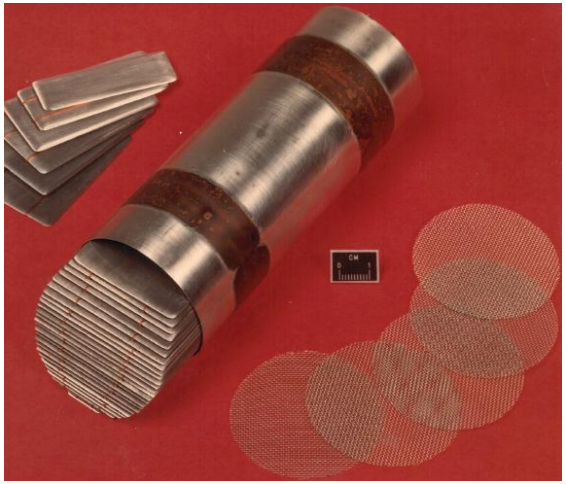
$\mu_0 \Delta H = 7$ T

$\Delta T = 14$ K (Gd alone)

$\Delta T = 47$ K (prototype)

improved in 1978

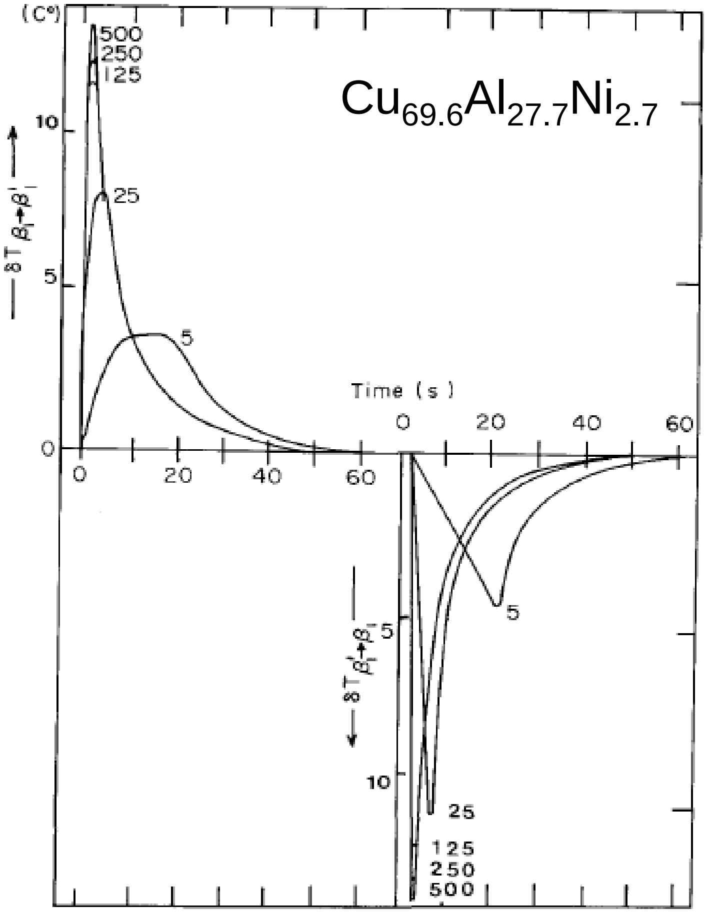
$\Delta T = 80$ K



Brown, JAP **47**, 3763 (1975)

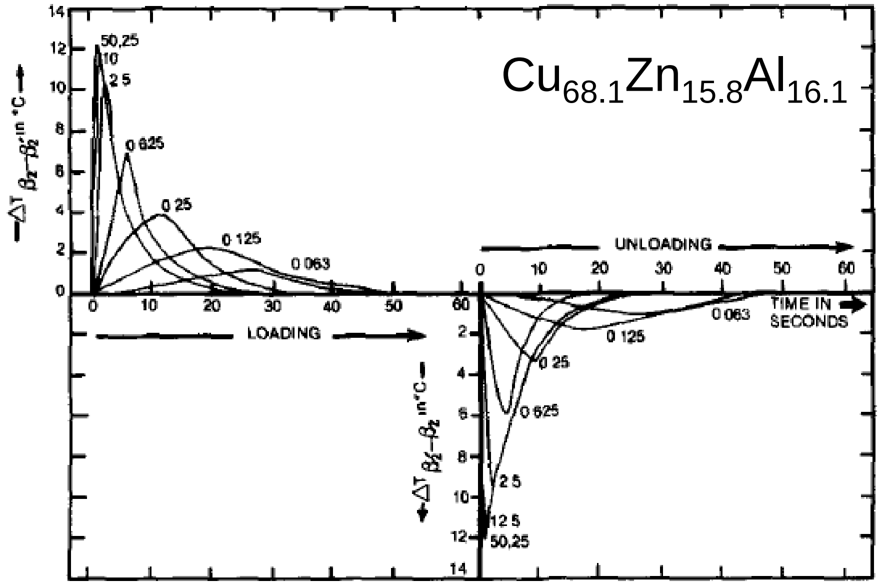
Discovery of giant eC effects

1st order structural phase transition, shape memory alloys



$Cu_{69.6}Al_{27.7}Ni_{2.7}$

Rodríguez and Brown,
Metall. Trans. A **11,** 147 (1980)

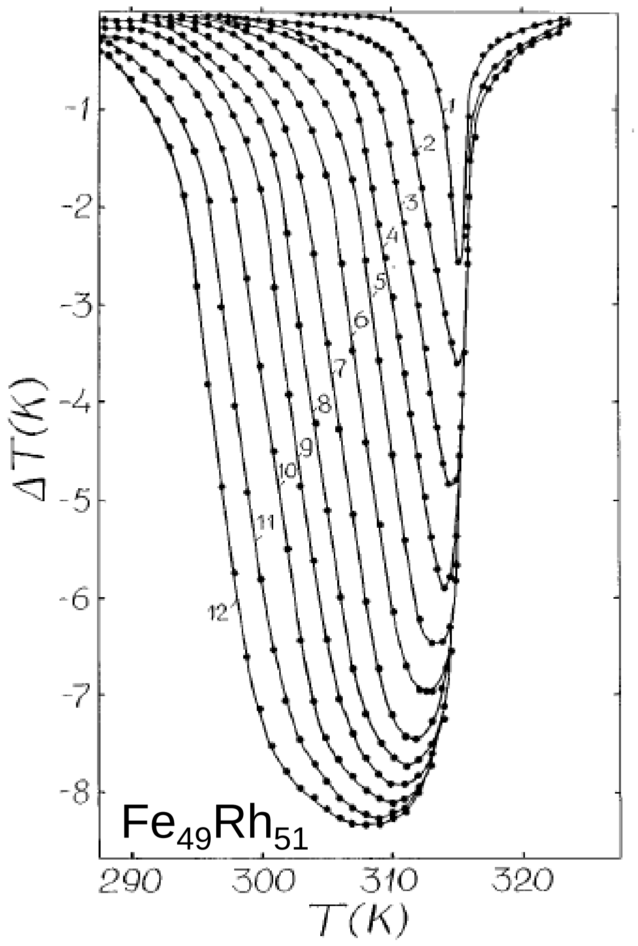


$Cu_{68.1}Zn_{15.8}Al_{16.1}$

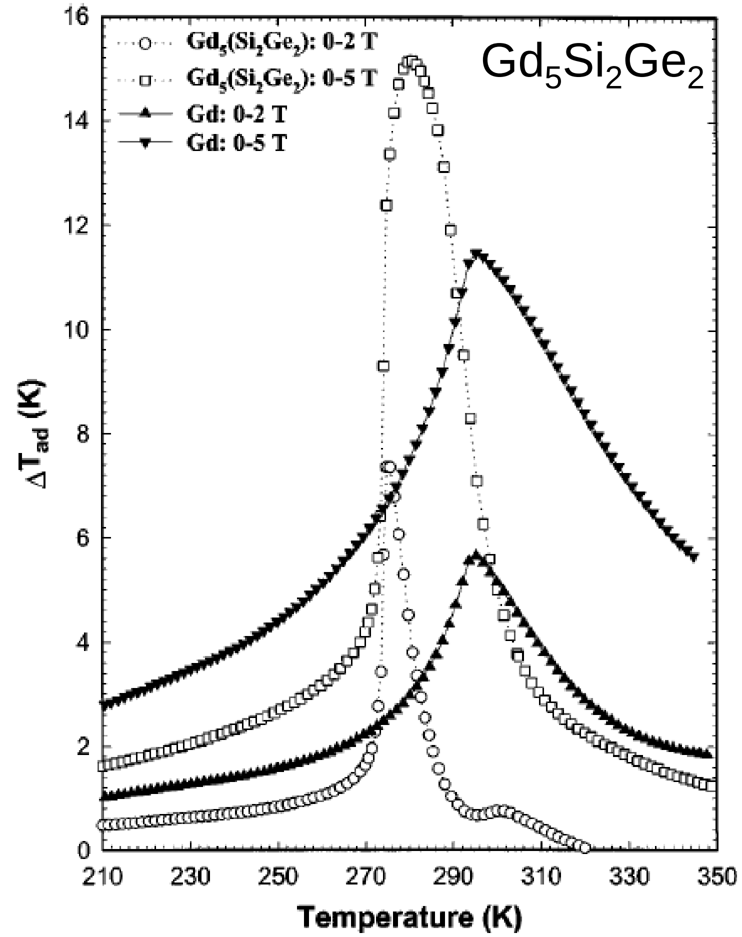
Brown, *Metall. Trans. A* **12,** 1491 (1981)

Giant MC effects near 1st order transitions

Metallic alloys near magnetostructural transitions



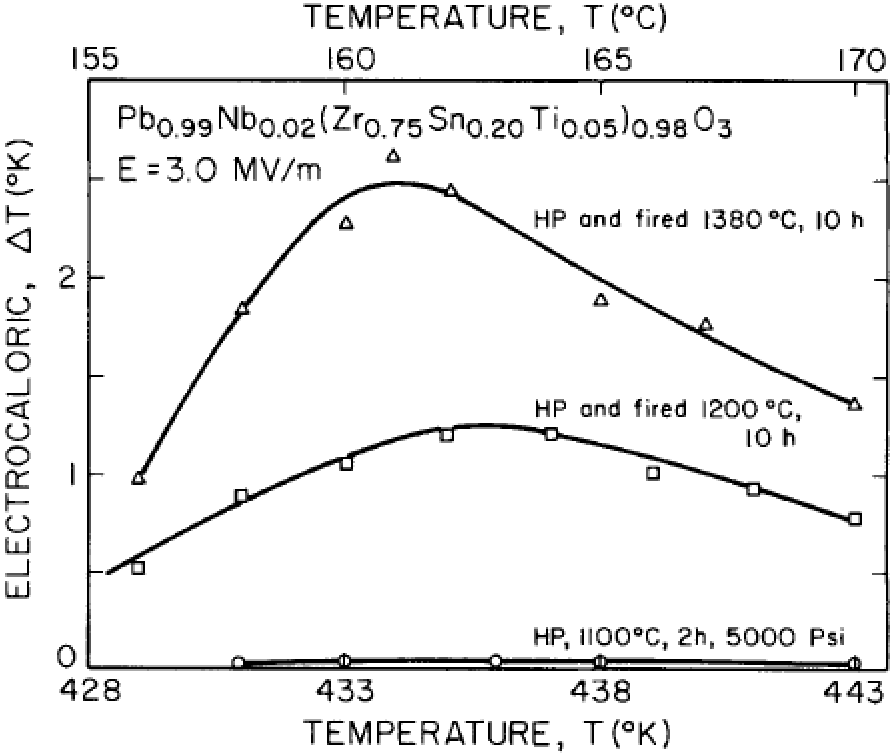
Nikitin *et al. Phys. Lett. A* **148,** 363 (1990)



Pecharsky and Gschneidner Jr.,
PRL **78,** 4494 (1997)

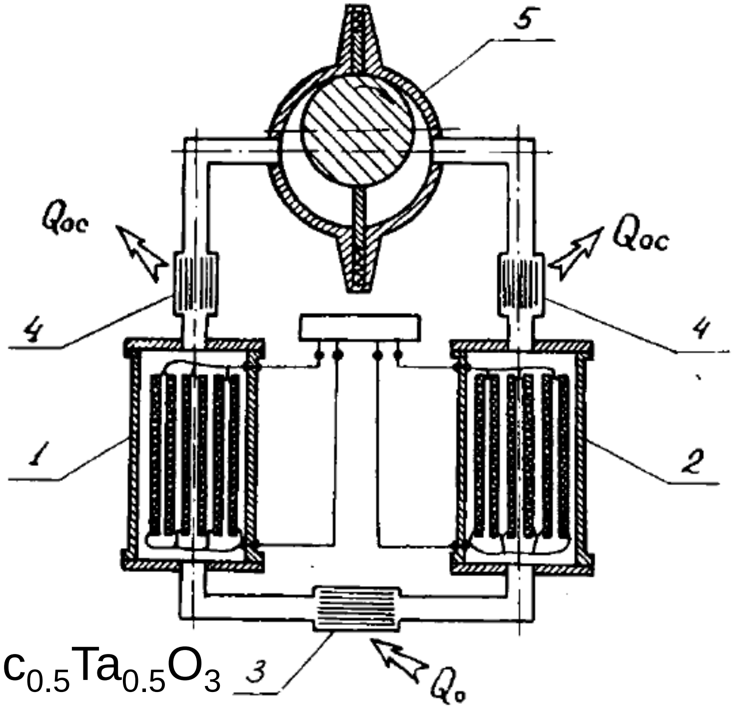
ECE near 1st order transitions

Small effects in bulk materials…



Tuttle and Payne, *Ferroelectrics* **37,** 603 (1981)

…but prototype developed



$PbSc_{0.5}Ta_{0.5}O_3$

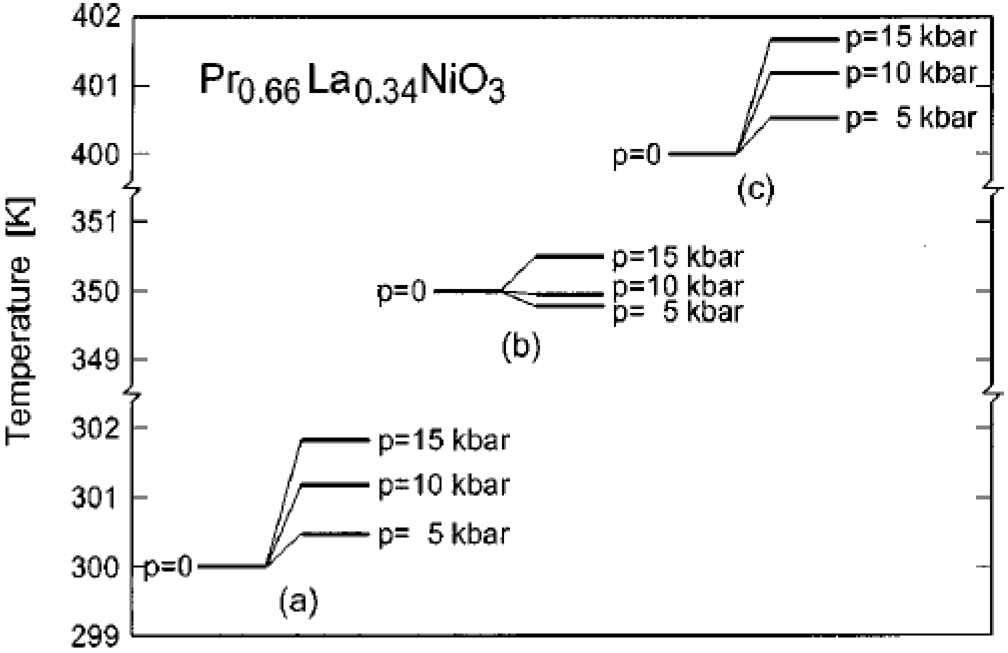
ΔE ~ 60 kV cm^{-1}

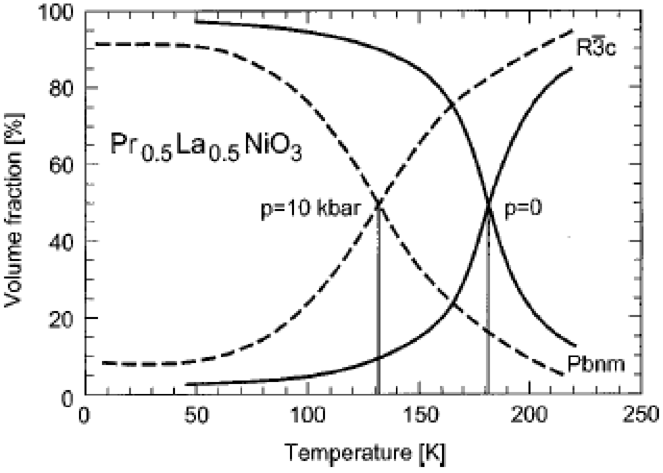
ΔT = 0.9 K (PST alone)

ΔT = 5 K (prototype)

Sinyavsky and Brodyansky,
Ferroelectrics **131,** 321 (1992)

Small BC effects near wide phase transitions





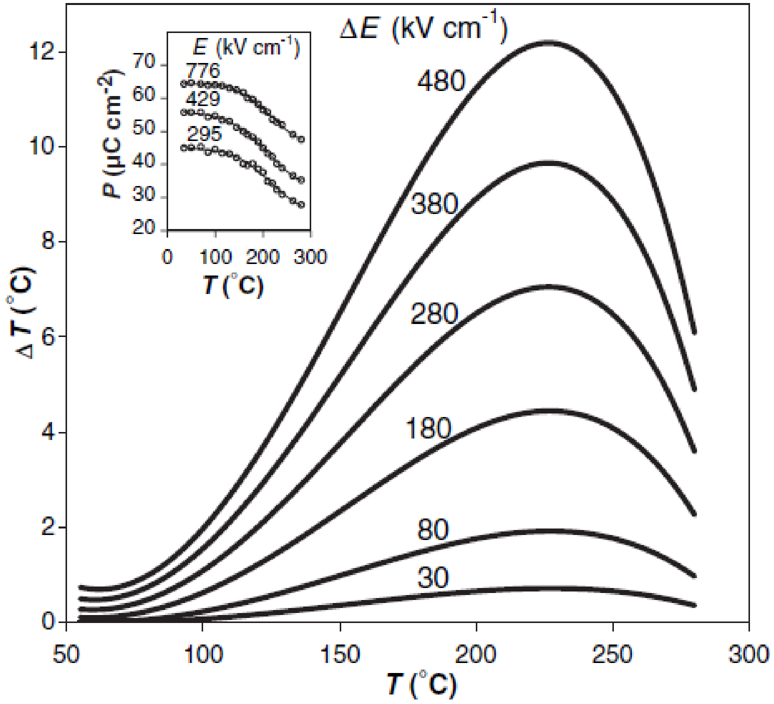
K. Alex Müller *et al.*, APL **73**, 1056 (1998)

elastic heating dwarfed BC effects arising from transition

Giant EC effects in thin films

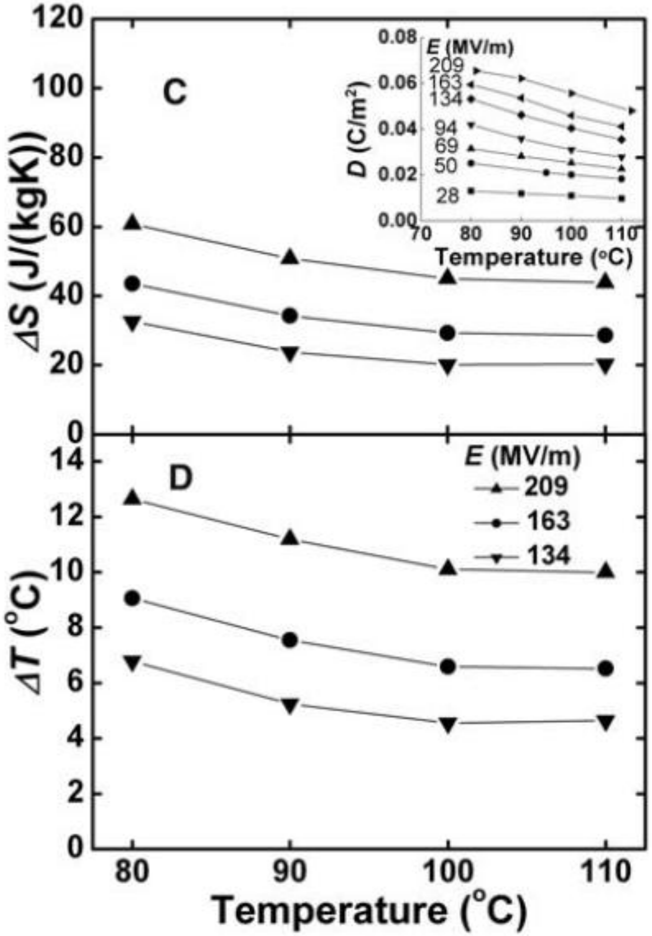
High breakdown fields in thin films

$PbZr_{0.95}Ti_{0.05}O_3$



Mischenko *et al. Science* **311,** 1270 (2006)

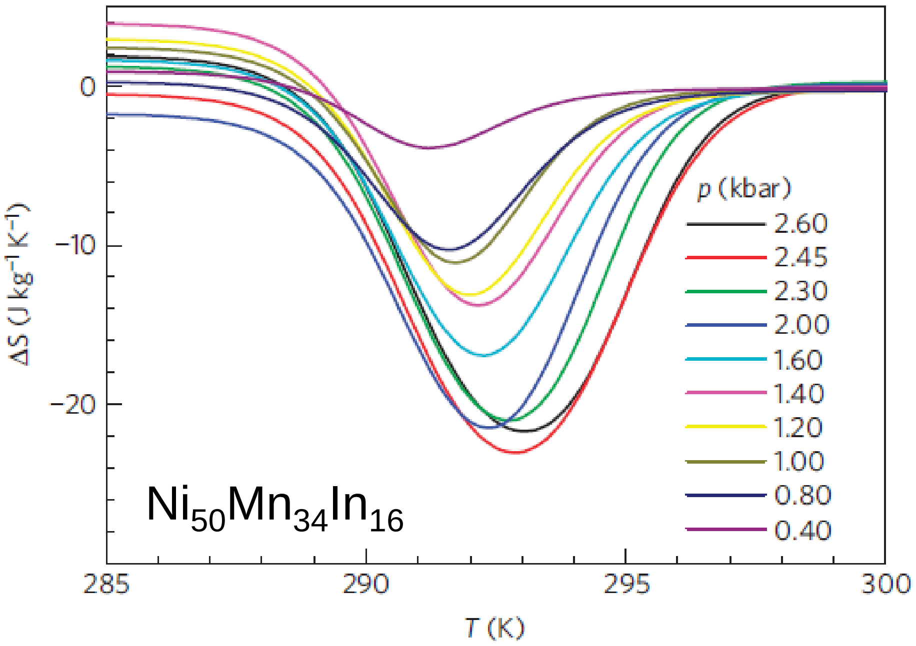
Fluorinated polymers



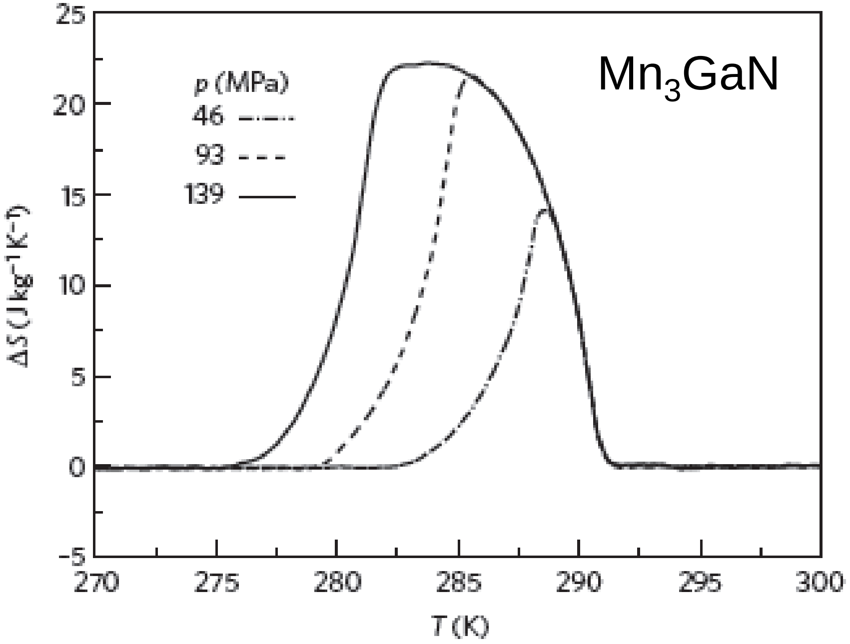
Neese *et al*. *Science* **321,** 821 (2008)

Giant BC effects near sharp phase transitions

Magnetic compounds near magnetostructural transitions



Mañosa *et al.*, *Nature Materials* **9**, 478 (2010)

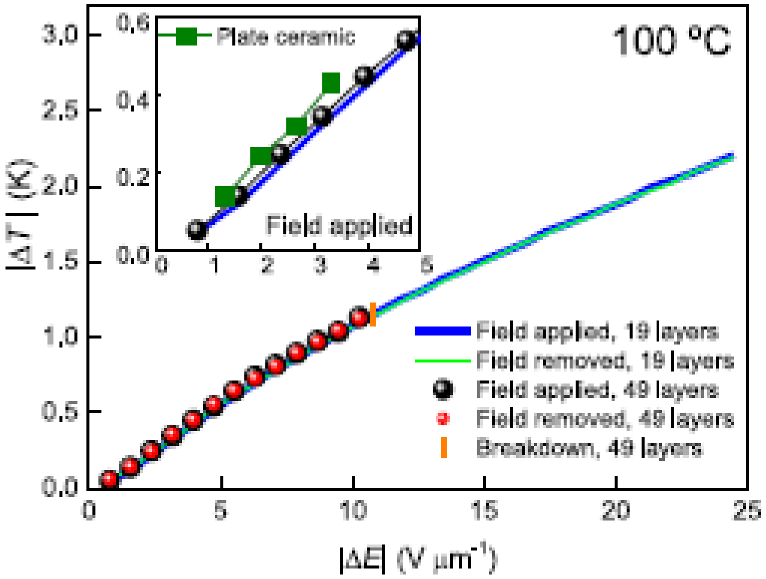


Matsunami *et al.*, *Nature Materials* **14**, 473 (2015)

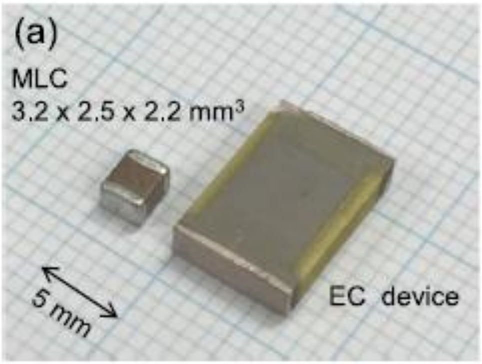
Giant EC effects in multilayer capacitors

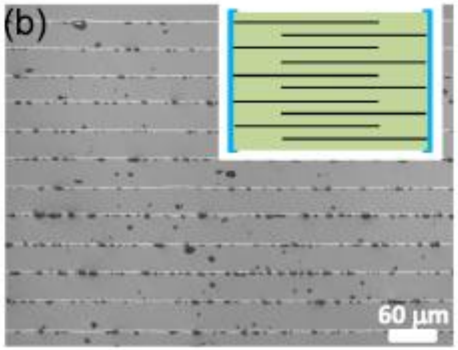
Best of bulk and thin-films:

- large EC effects
- good thermal transfer
- small voltages
- no inert substrate



0.9 PMN – 0.1 PT





muRata
INNOVATOR IN ELECTRONICS

Hirose *et al.* APL Materials **4,** 064105 (2016)

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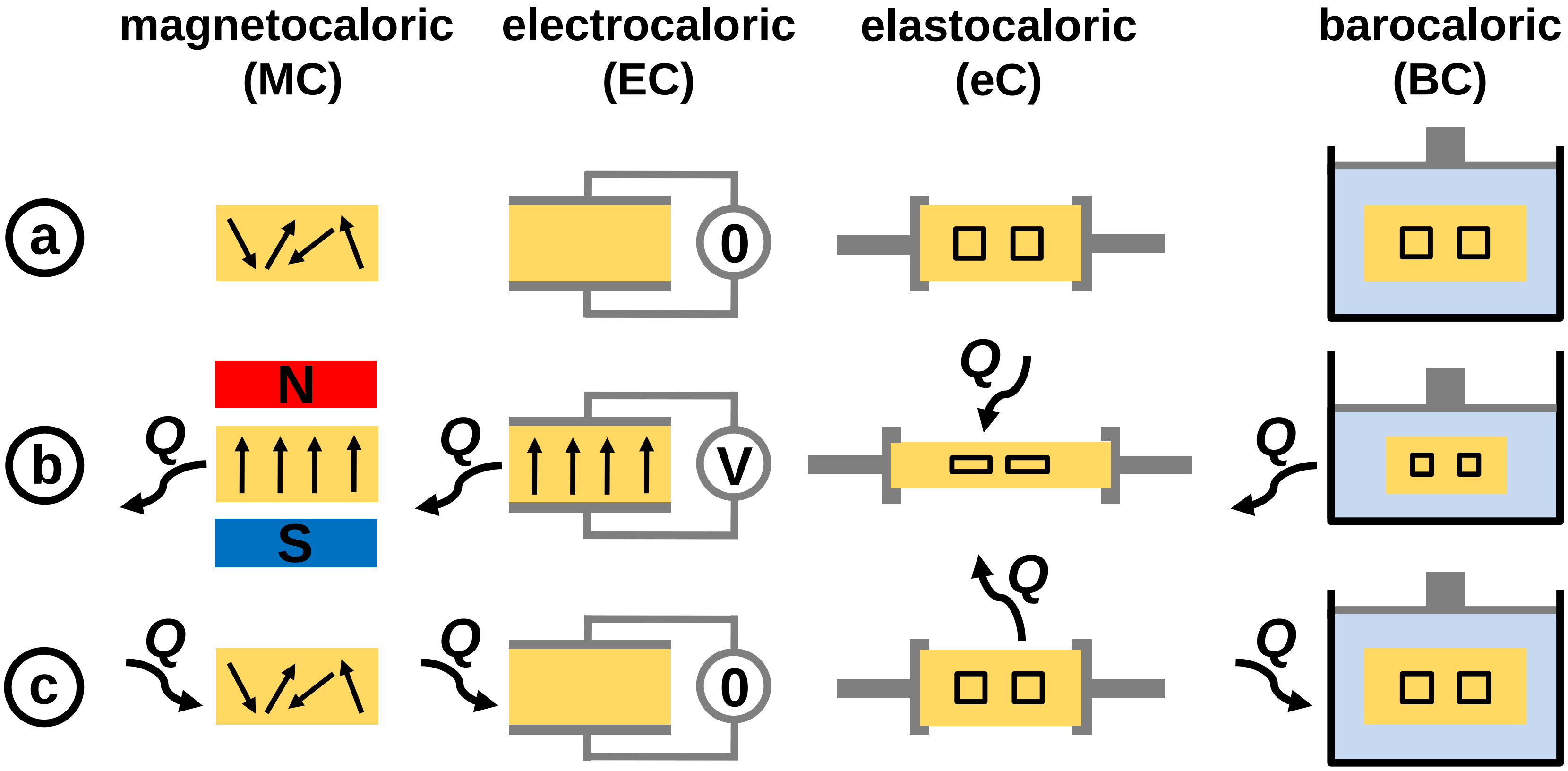
Caloric materials



$Q = T\Delta S\ (\approx -c\Delta T)$

Moya *et al.*, *Nature Materials* **13**, 439 (2014)

Crossley *et al.*, AIP *Advances* **5**, 067153 (2015)

Stern-Taulats *et al.* MRS Bulletin **43**, 295 (2018)

Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_H \mathrm{d}T + \left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H$$

Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_H \mathrm{d}T + \left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H$$

$$\frac{C}{T} = \left(\frac{\partial S}{\partial T}\right)_H$$

Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

$$\mathrm{d}S = \frac{C}{T}\,\mathrm{d}T + \left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H$$

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Thermodynamics

e.g. magnetocaloric effect

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$$\frac{C}{T} = \left(\frac{\partial S}{\partial T}\right)_H$$

Maxwell relation: $$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T$$

Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

$$\mathrm{d}S = \frac{C}{T}\mathrm{d}T + \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

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Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

$$\mathrm{d}S = \frac{C}{T}\mathrm{d}T + \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

Isothermal conditions: $\mathrm{d}T = 0$

$$\mathrm{d}S = \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

$$\boxed{\Delta S = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right)_{H'} \mathrm{d}H'}$$

Thermodynamics

e.g. magnetocaloric effect

$$S = S(T, H)$$

$$\mathrm{d}S = \frac{C}{T}\mathrm{d}T + \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

Adiabatic conditions: $\mathrm{d}S = 0$

$$\mathrm{d}T = -\frac{T}{C}\left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

$$\boxed{\Delta T = -\int_{H_1}^{H_2} \frac{T}{C}\left(\frac{\partial M}{\partial T}\right)_{H'} \mathrm{d}H'}$$

Thermodynamics

straightforward to extend to other calorics

$$S = S(T, E)$$

$$\mathrm{d}S = \frac{C}{T}\mathrm{d}T + \left(\frac{\partial P}{\partial T}\right)_E \mathrm{d}E$$

Isothermal conditions: $\mathrm{d}T = 0$

$$\mathrm{d}S = \left(\frac{\partial P}{\partial T}\right)_E \mathrm{d}E$$

$$\boxed{\Delta S = \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T}\right)_{E'} \mathrm{d}E'}$$

Thermodynamics

straightforward to extend to other calorics

$$S = S(T, E)$$

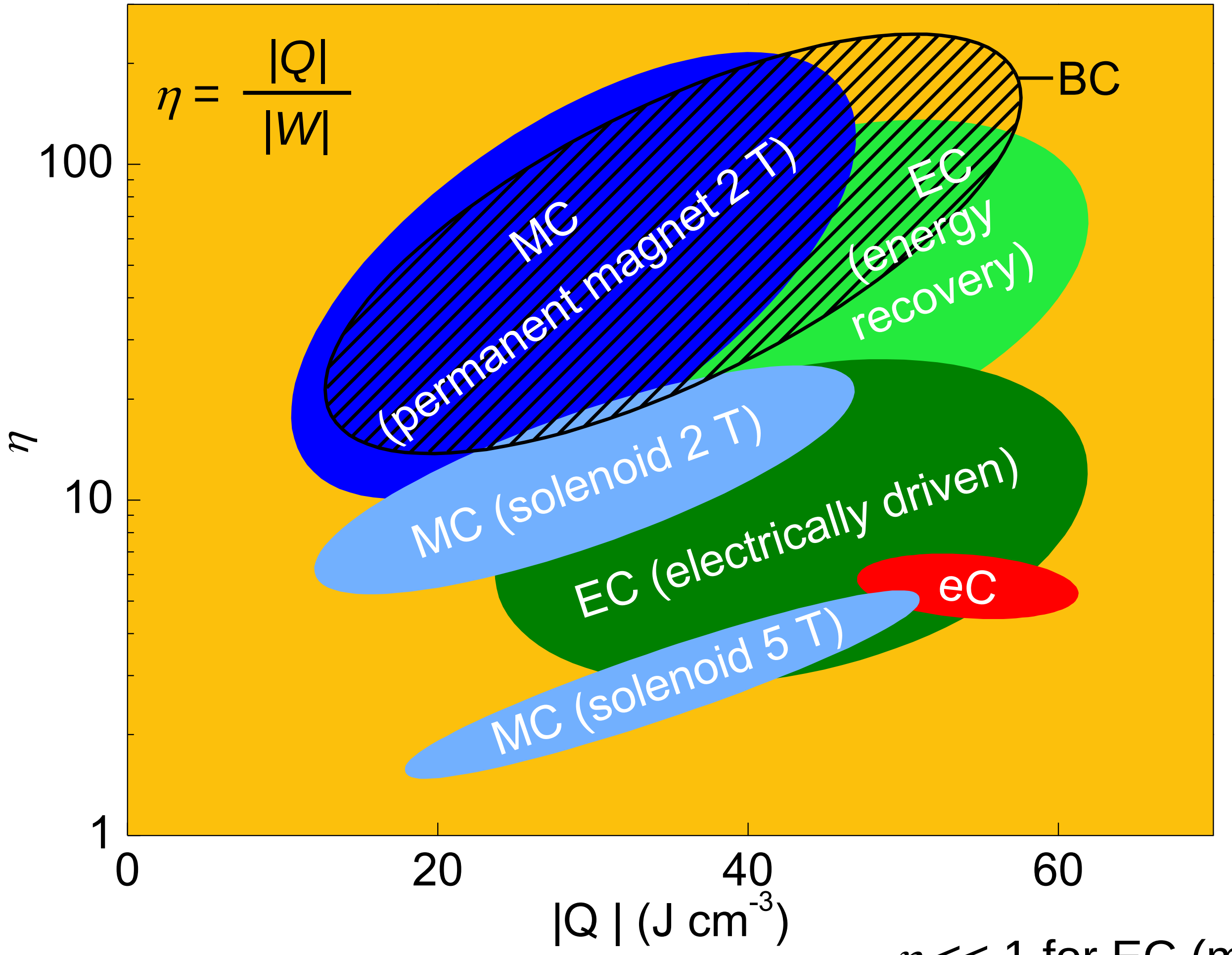
$$\mathrm{d}S = \frac{C}{T}\mathrm{d}T + \left(\frac{\partial P}{\partial T}\right)_E \mathrm{d}E$$

Adiabatic conditions: $\mathrm{d}S = 0$

$$\mathrm{d}T = -\frac{T}{C}\left(\frac{\partial P}{\partial T}\right)_E \mathrm{d}E$$

$$\boxed{\Delta T = -\int_{E_1}^{E_2} \frac{T}{C}\left(\frac{\partial P}{\partial T}\right)_{E'} \mathrm{d}E'}$$

Energy efficiency of caloric materials



η << 1 for EC (mechanical)

Defay *et al.*, *Advanced Materials* **25**, 3337 (2013)
Moya *et al. Nature Physics* **11**, 439 (2015)
Crossley *et al.*, *AIP Advances* **5**, 067153 (2015)

Measuring caloric effects

	Direct measurements	Indirect measurements
Q & ΔS	Calorimetric measurements	Maxwell relation Clausius-Clapeyron (1st order)
ΔT	Temperature measurements	

Maxwell relation:

$$\Delta S = \int_0^Y \left(\frac{\partial X}{\partial T}\right)_{Y'} dY'$$

$$Q = T\Delta S$$

$$\Delta T = -\frac{T}{C}\Delta S$$

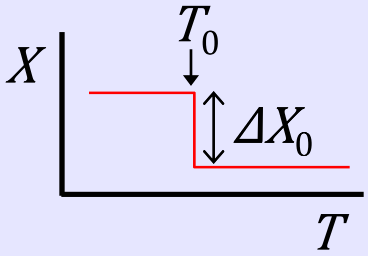
$X = M, P, -v \quad Y = \mu_0 H, E, p$

Clausius-Clapeyron:

$$\frac{dT_0}{dY} = -\frac{\Delta X_0}{\Delta S_0}$$

$X_0 = M, P, -v$

$Y = \mu_0 H, E, p$

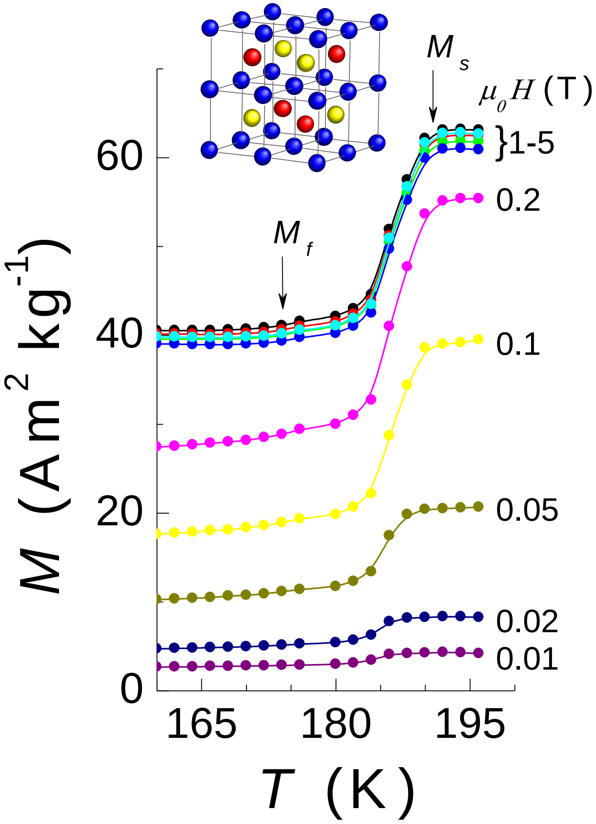


Largest near 1st order phase transitions

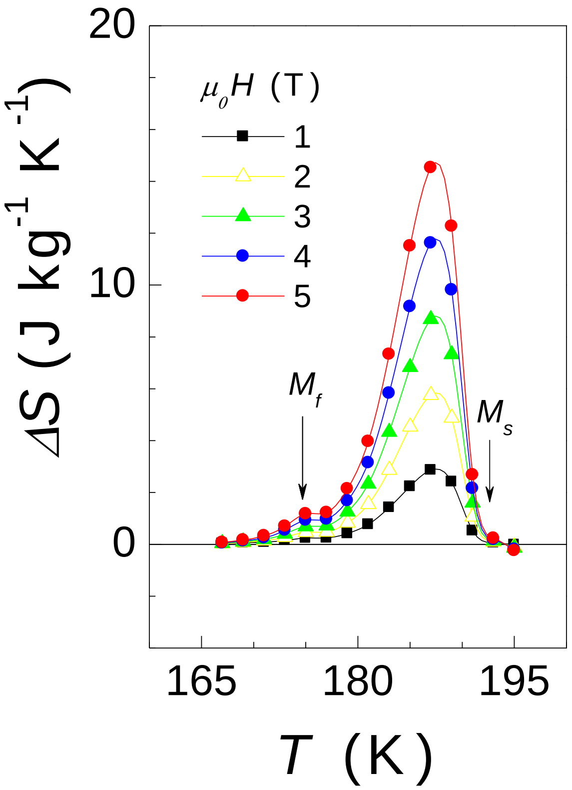
Indirect measurements

e.g. magnetocaloric effect: measure $M(H,T)$

$Ni_{50}Mn_{35}Sn_{15}$



$$\Delta S = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'$$



$\Delta S > 0$
on applying field

Inverse MC effect

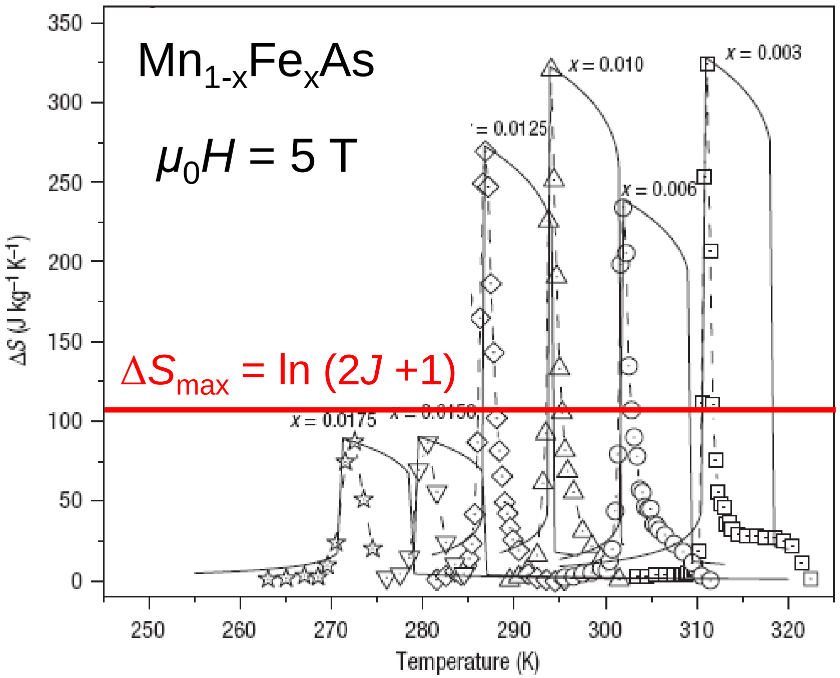
Krenke *et al.*, *Nature Materials* **4**, 450 (2005)

Mind the protocol

Maxwell relation method:

Overestimation (strongly hysteretic) first-order transitions

e.g. Magnetocalorics



de Campos *et al.*, *Nature Materials* **5**, 802 (2006)

Indirect method:

Correct probing (hysteresis)

$\Delta S = 35$ J K^{-1} kg^{-1} ($\mu_0 H = 5$ T)

Caron *et al.*, JMMM **321**, 3559 (2009)

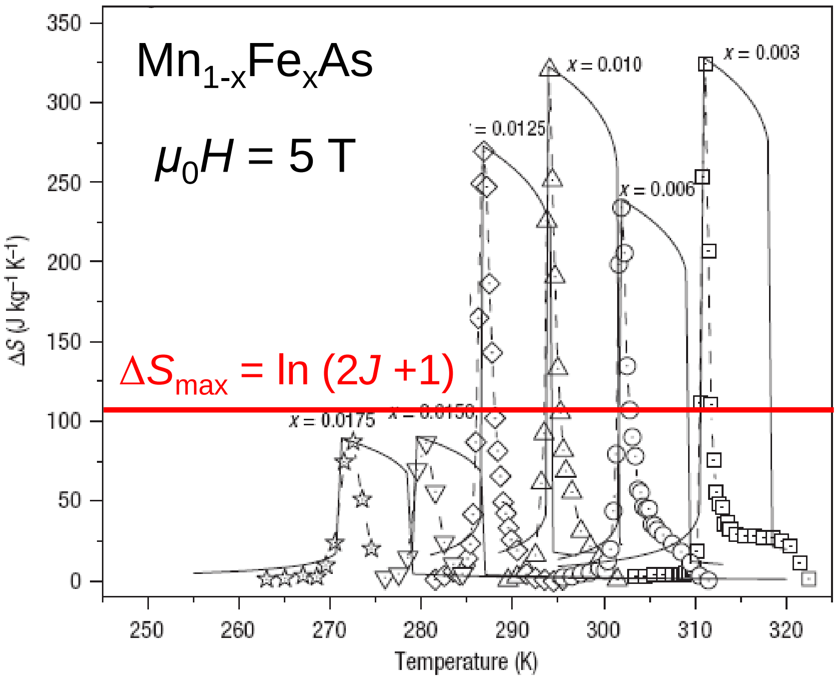
Balli *et al.*, APL **95**, 072509 (2009)

Mind the protocol

Maxwell relation method:

Overestimation (strongly hysteretic) first-order transitions

e.g. Magnetocalorics

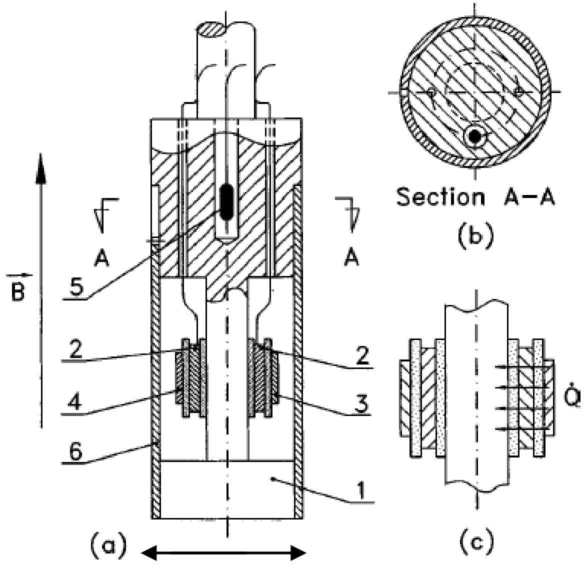


> “In this house we obey the laws of Thermodynamics”.

Homer J. Simpson (1995)

de Campos *et al.*, *Nature Materials* **5**, 802 (2006)

Calorimetry in magnetic field



1 Cu block
2 Sensors (thermobatteries)
3 Sample
4 Reference
5 Carbon-glass resistor (*T*)

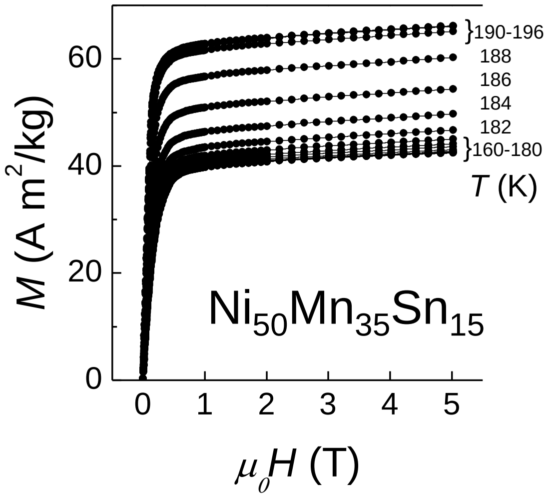
T sweep at constant *H*

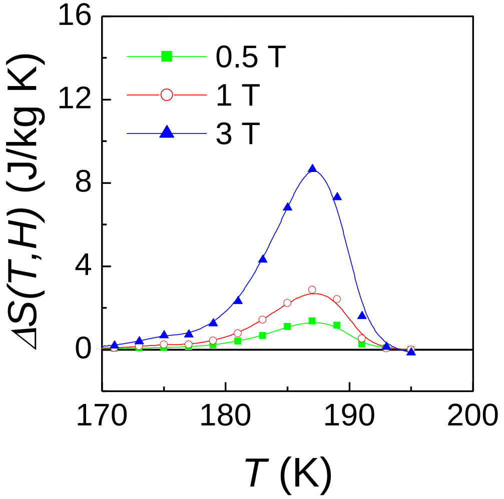
H sweep at constant *T*

Marcos *et al.*, *Rev. Sci. Inst.* **74**, 4768 (2003)

Quasi-direct versus indirect

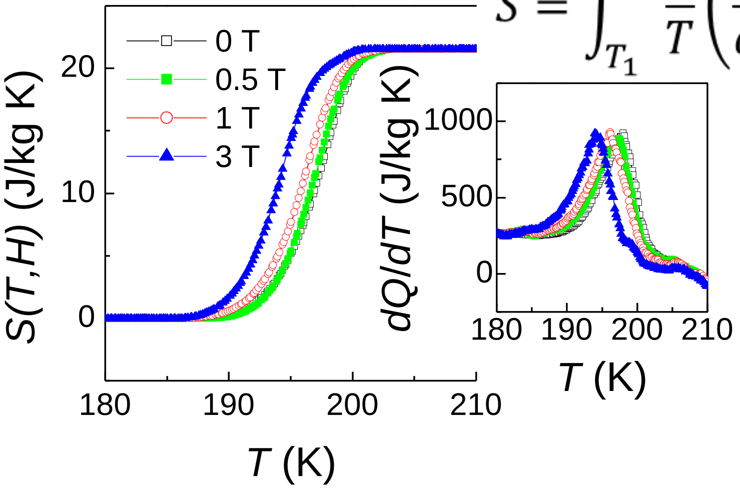
Magnetic measurements

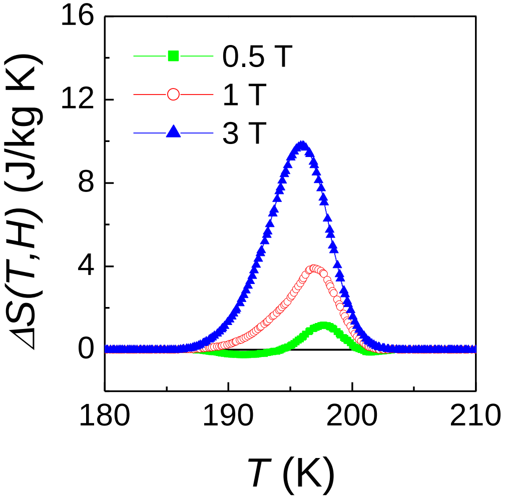




Calorimetric measurements

$$S = \int_{T_1}^{T_2} \frac{1}{T}\left(\frac{dQ}{dT}\right) dT$$

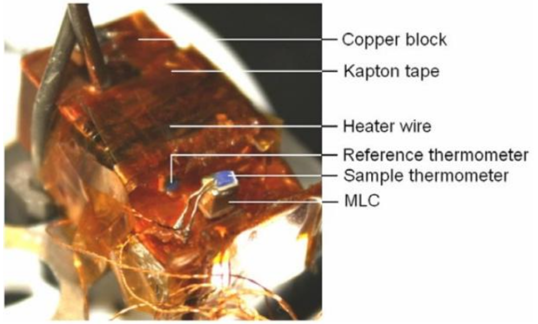


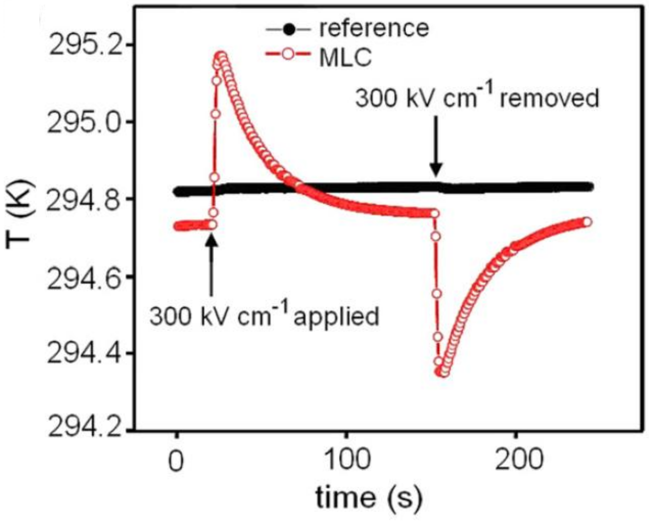


Moya *et al.*, JMMM **316**, e572 (2007) & *Adv. Mater.* **21**, 1 (2009)

Thermometry in external field: EC effects

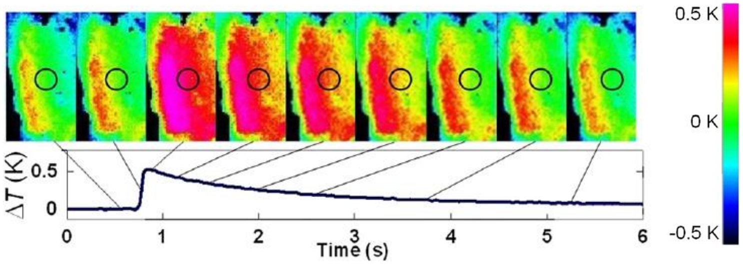
Standard thermometry



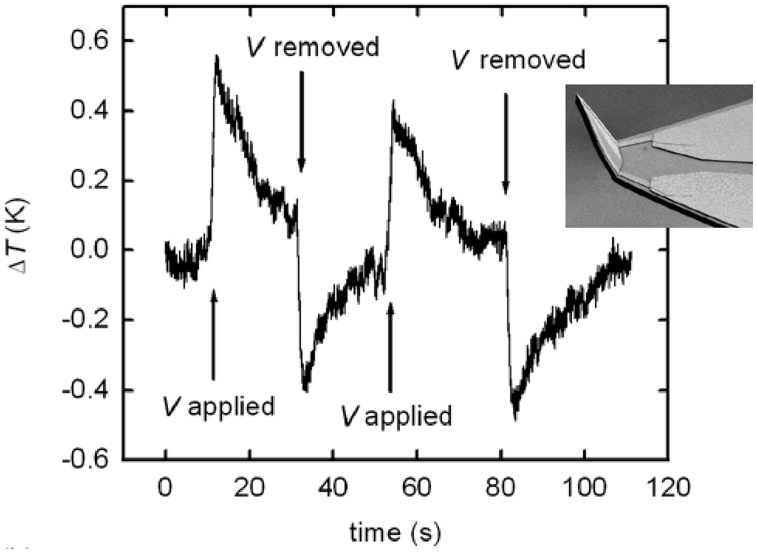


Kar-Narayan *et al.*,
J. Phys. D: Appl. Phys. **43**, 032002 (2010)

Infra-red imaging



Scanning thermal microscopy



Kar-Narayan *et al.*,
APL **102**, 032903 (2013)

Oxide multicalorics

Background

Brief history of calorics

Thermodynamics and measurements

Multicaloric $BaTiO_3$

Multicaloric $(NH_4)_2SO_4$

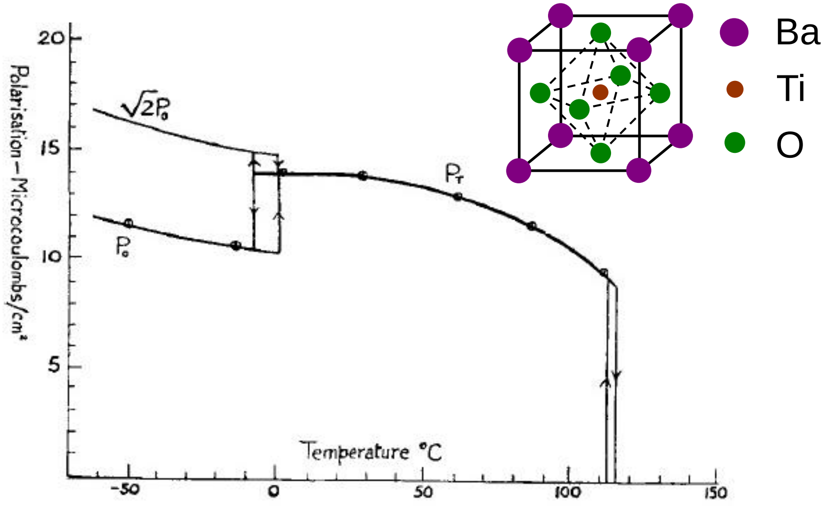
Colossal barocaloric plastic crystals

Ferroelectric phase transitions in BaTiO$_3$

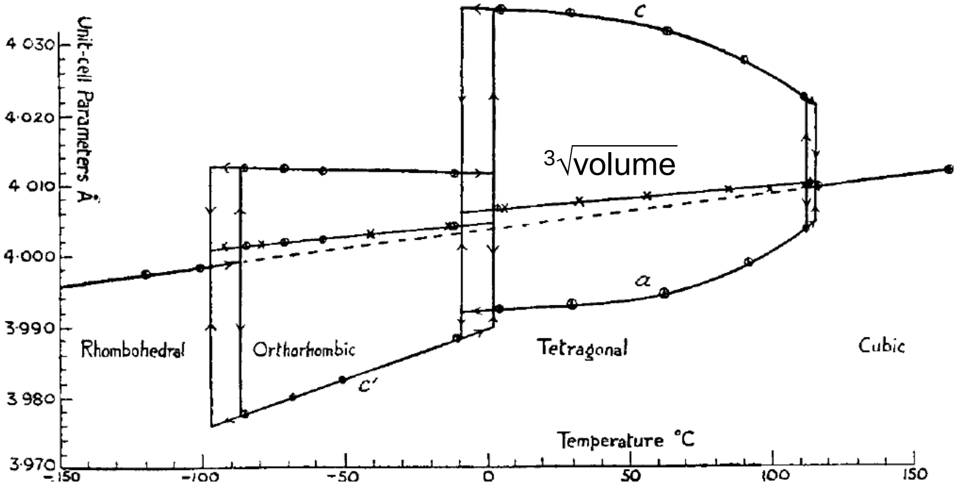
Very sharp first-order transitions

Large changes in polarization

Small changes in volume



Kay & Vousden, *Phil. Mag.* **40**, 1010 (1949)



Electrocaloric effects

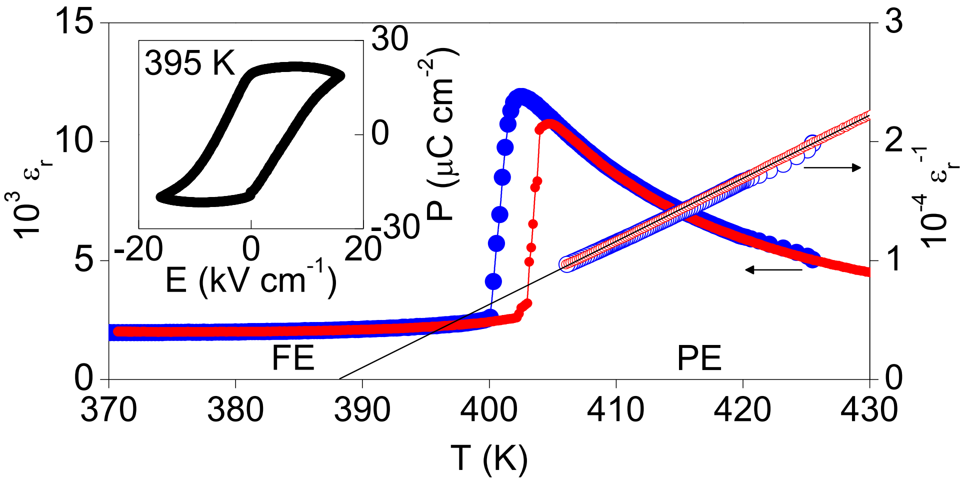
Barocaloric effects

$$\frac{dT_0}{dE} = -\frac{\Delta P_0}{\Delta S_0} > 0$$

$$\frac{dT_0}{dp} = \frac{\Delta v_0}{\Delta S_0} < 0$$

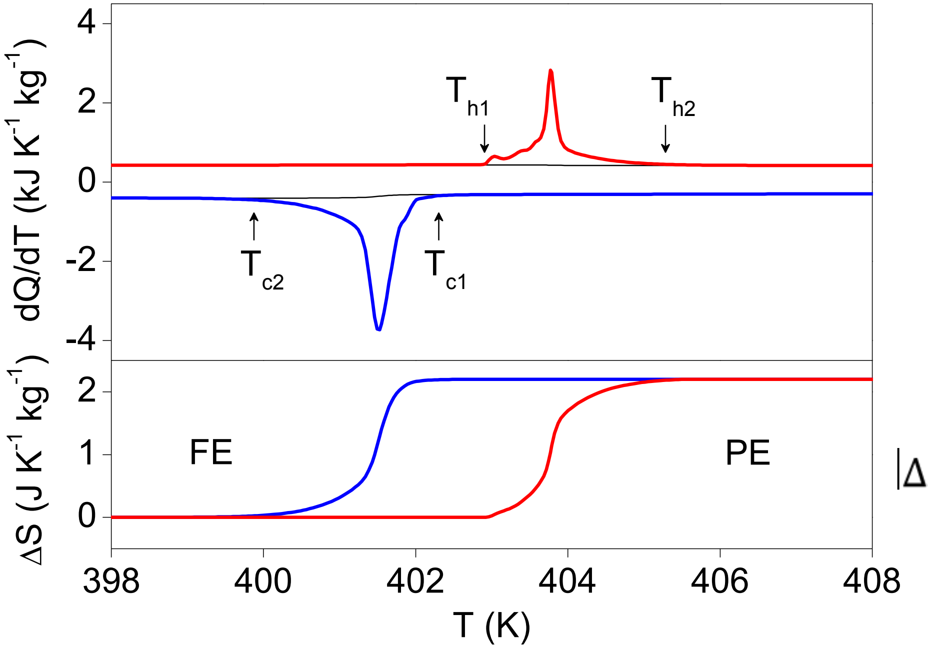
Cubic-tetragonal transition $BaTiO_3$

Dielectric
&
Ferroelectric
measurements



BTO single crystal (sc)

Calorimetric
measurements

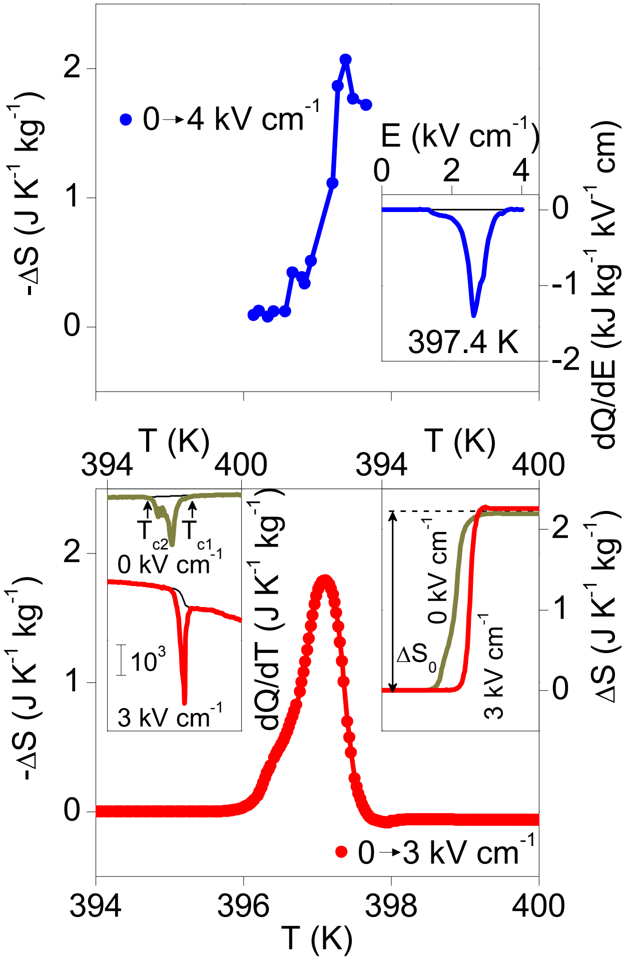


$$|Q_0| = \int_{T_1}^{T_2} \left(\frac{dQ}{dT}\right) dT = 890\pm90 \text{ J kg}^{-1}$$

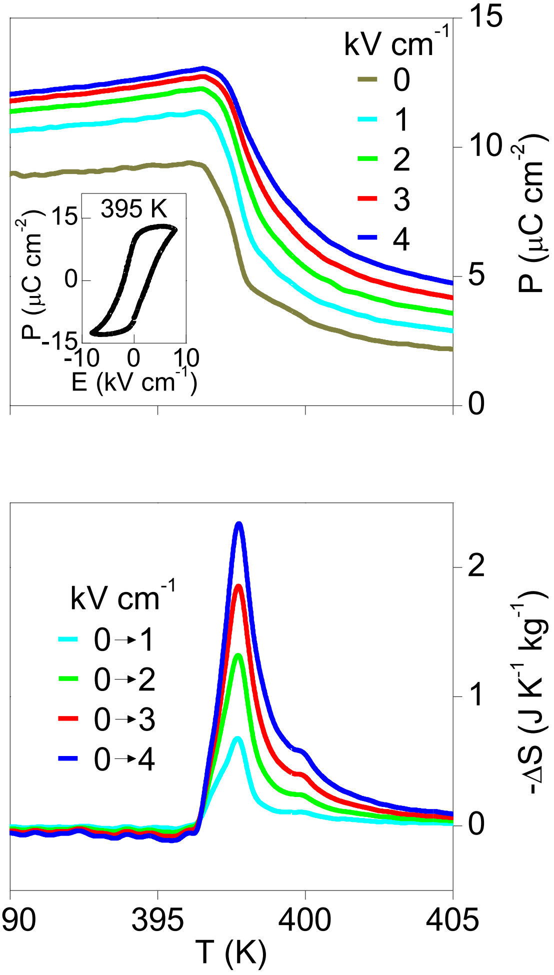
$$|\Delta S_0| = \int_{T_1}^{T_2} \frac{1}{T}\left(\frac{dQ}{dT}\right) dT = 2.2\pm0.2 \text{ J K}^{-1} \text{ kg}^{-1}$$

EC effect cubic-tetragonal transition

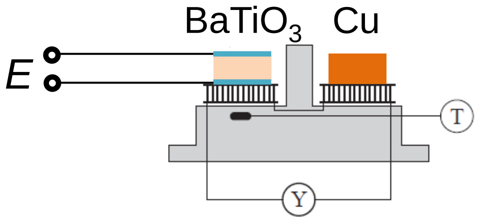
Direct & quasi-direct



Indirect



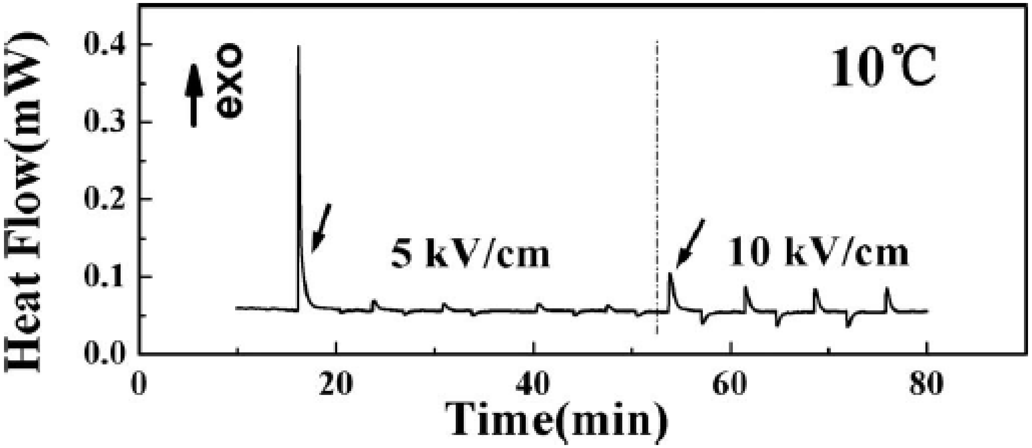
BTO single crystal (sc)



$$\Delta S = \frac{1}{\rho}\int_0^E \left(\frac{\partial P}{\partial T}\right)_{E'} dE'$$

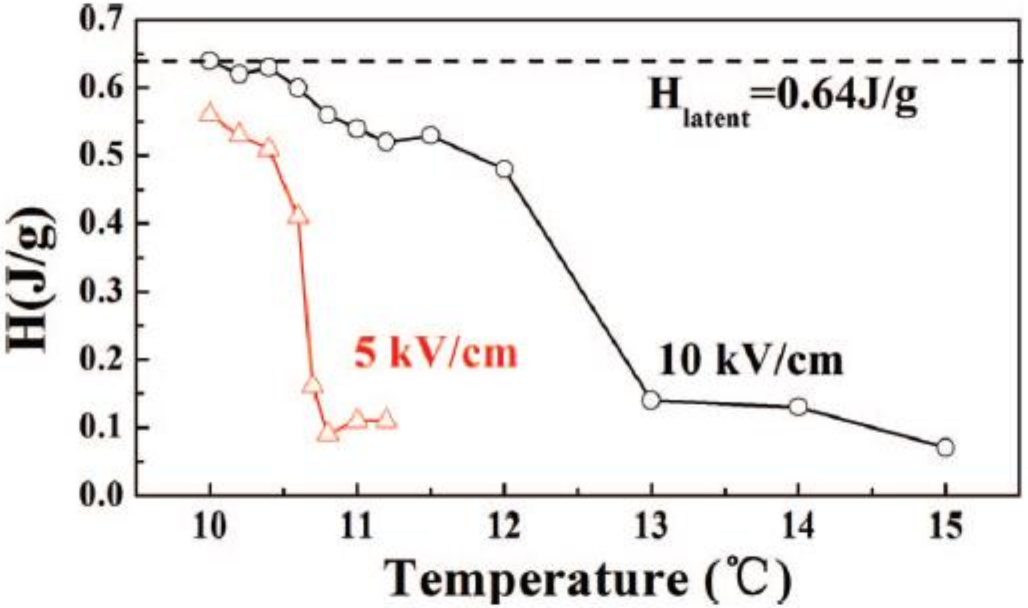
X. Moya *et al. Adv. Mat.* **25**, 1360 (2013)

EC effect tetragonal-orthorhombic transition



BTO single crystal (sc)

Calorimetric measurements



$\Delta S_0 = - 2.3\ \mathrm{J\ K^{-1}\ kg^{-1}}$

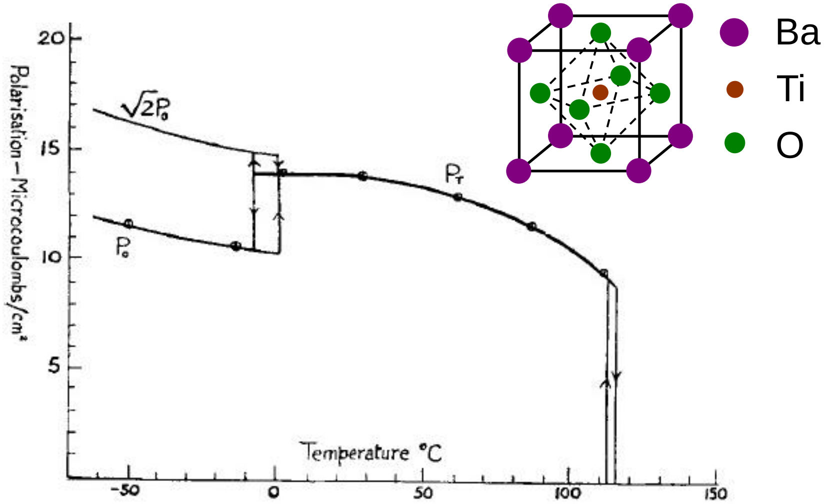
Y. Bai *et al. AIP Advances* **2**, 022162 (2012)

Ferroelectric phase transitions in $BaTiO_3$

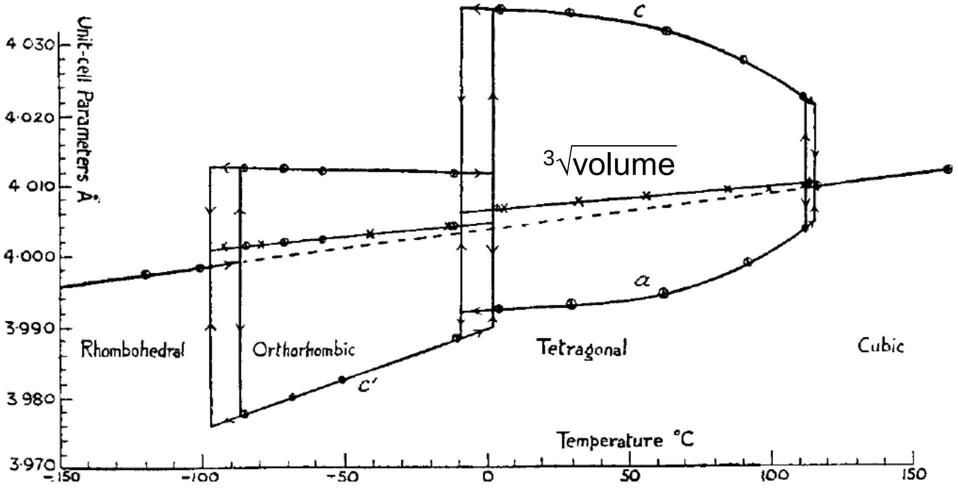
Very sharp first-order transitions

Large changes in polarization

Small changes in volume



Kay & Vousden, *Phil. Mag.* **40**, 1010 (1949)



Electrocaloric effects

Barocaloric effects

$$\frac{dT_0}{dE} = -\frac{\Delta P_0}{\Delta S_0} > 0$$

$$\frac{dT_0}{dp} = \frac{\Delta v_0}{\Delta S_0} < 0$$

Ferroelectric phase transitions in $BaTiO_3$

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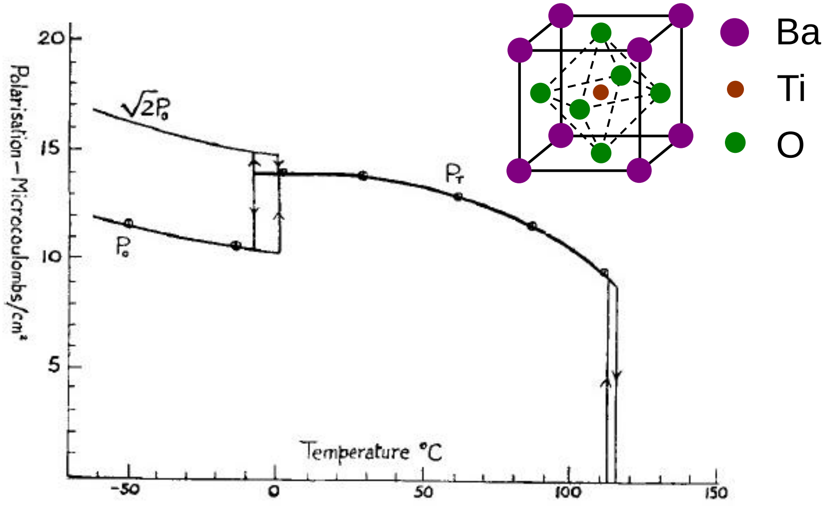
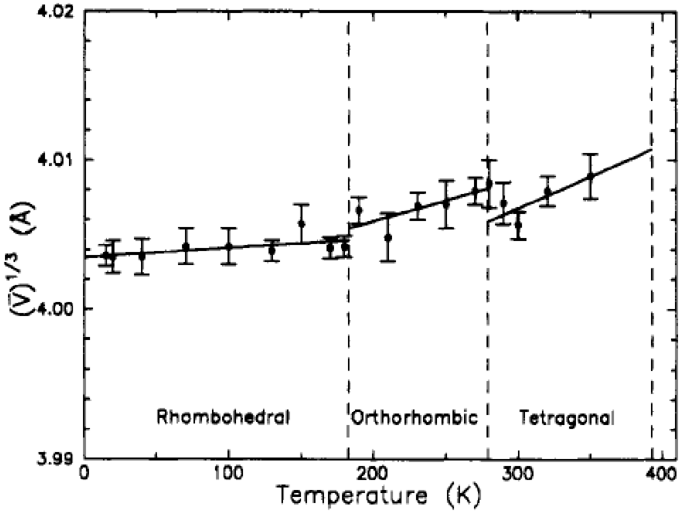


Kay & Vousden, Phil. Mag. **40**, 1010 (1949)

Small changes in volume



Kwei et al., *J. Phys. Chem.* **97**, 2368 (1993)

Electrocaloric effects

$$\frac{dT_0}{dE} = -\frac{\Delta P_0}{\Delta S_0} > 0$$

Barocaloric effects

$$\frac{dT_0}{dp} = \frac{\Delta v_0}{\Delta S_0} < 0$$

Giant barocaloric materials

Giant BC material	***T*** **K**	**|Δ*S*|** **J K^{-1} kg^{-1}**	**|*Q*|** **kJ kg^{-1}**	**|Δ*p*|** **GPa**	**|Δ*S*/Δ*p*|** **J K^{-1} kg^{-1} GPa^{-1}**	**|*Q*/Δ*p*|** **kJ kg^{-1} GPa^{-1}**	**Reference**
Ni-Mn-In	293	24	7.1	0.26	92.3	27.3	1
$Gd_5Si_2Ge_2$	270	11	2.9	0.20	55	14.5	2
La-Fe-Co-Si	237	8.7	2.0	0.20	43.5	10	3
$Fe_{49}Rh_{51}$	308	12.5	3.8	0.11	114	34.5	4
Mn_3GaN	285	21.6	6.2	0.09	232	66.2	5

Only in few expensive magnetic materials

(near magnetostructural phase transitions)

[1] Mañosa *et al.*, *Nat. Mater.* **9**, 478 (2010)

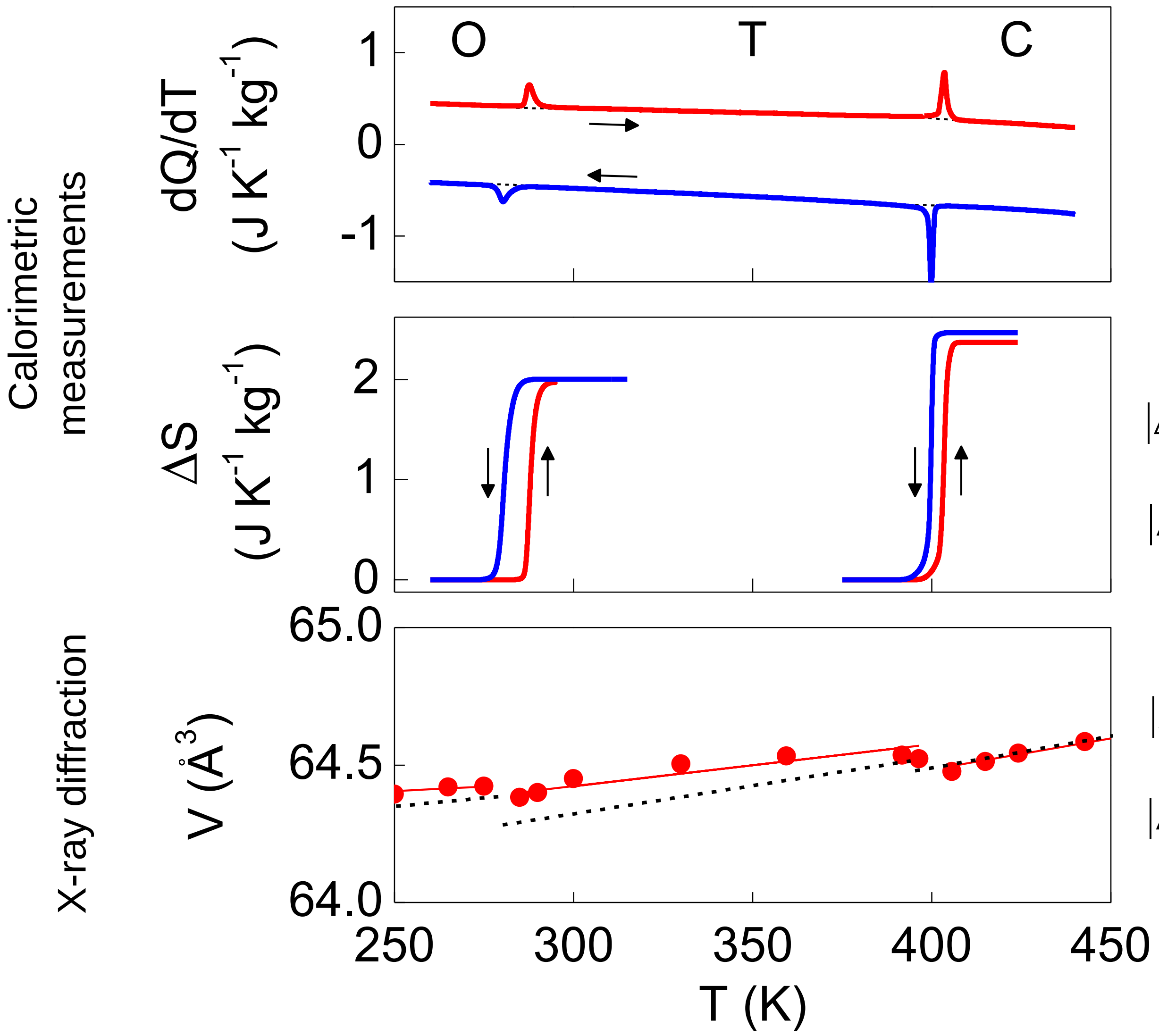
[2] Yuce *et al.*, APL **101**, 071906 (2012)

[3] Mañosa *et al.*, *Nat. Commun.* **2**, 592 (2011)

[4] Stern-Taulats *et al.*, PRB **89**, 214105 (2014)

[5] Matsunami *et al.*, *Nat. Mater.* **14**, 73 (2014)

Ferroelectric phase transitions in $BaTiO_3$



BTO polycrystal

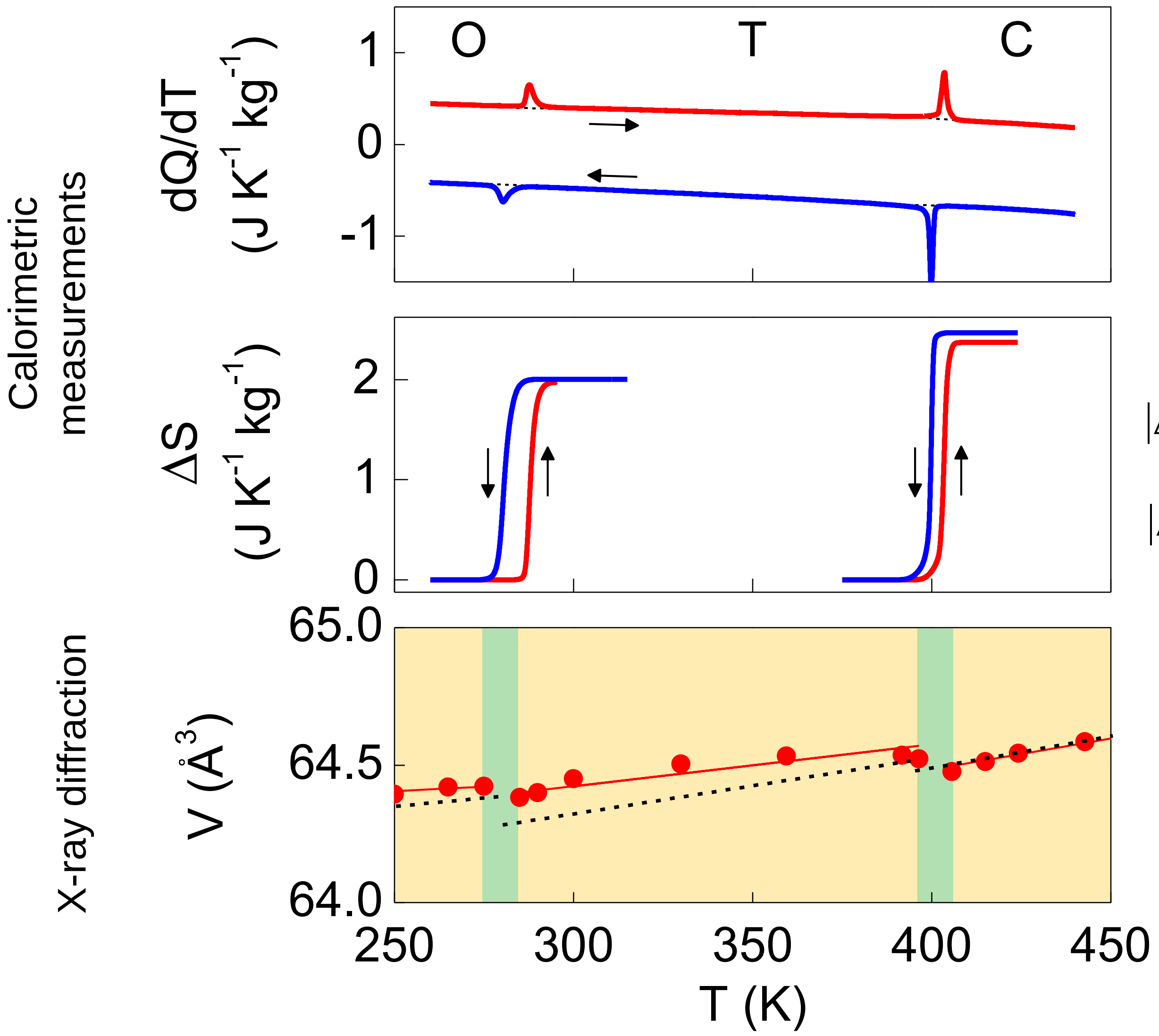
$|\Delta S_0^{C\text{-}T}| = 2.4 \pm 0.2$ J K^{-1} kg^{-1}

$|\Delta S_0^{T\text{-}O}| = 2.0 \pm 0.2$ J K^{-1} kg^{-1}

$|\Delta V_0^{C\text{-}T}/V_0^{C}| = 0.17 \pm 0.03$ %

$|\Delta V_0^{T\text{-}O} / V_0^{T}| = 0.06 \pm 0.01$ %

Ferroelectric phase transitions in $BaTiO_3$



BTO polycrystal

$|\Delta S_0^{\text{C-T}}| = 2.4 \pm 0.2\ \text{J K}^{-1}\ \text{kg}^{-1}$

$|\Delta S_0^{\text{T-O}}| = 2.0 \pm 0.2\ \text{J K}^{-1}\ \text{kg}^{-1}$

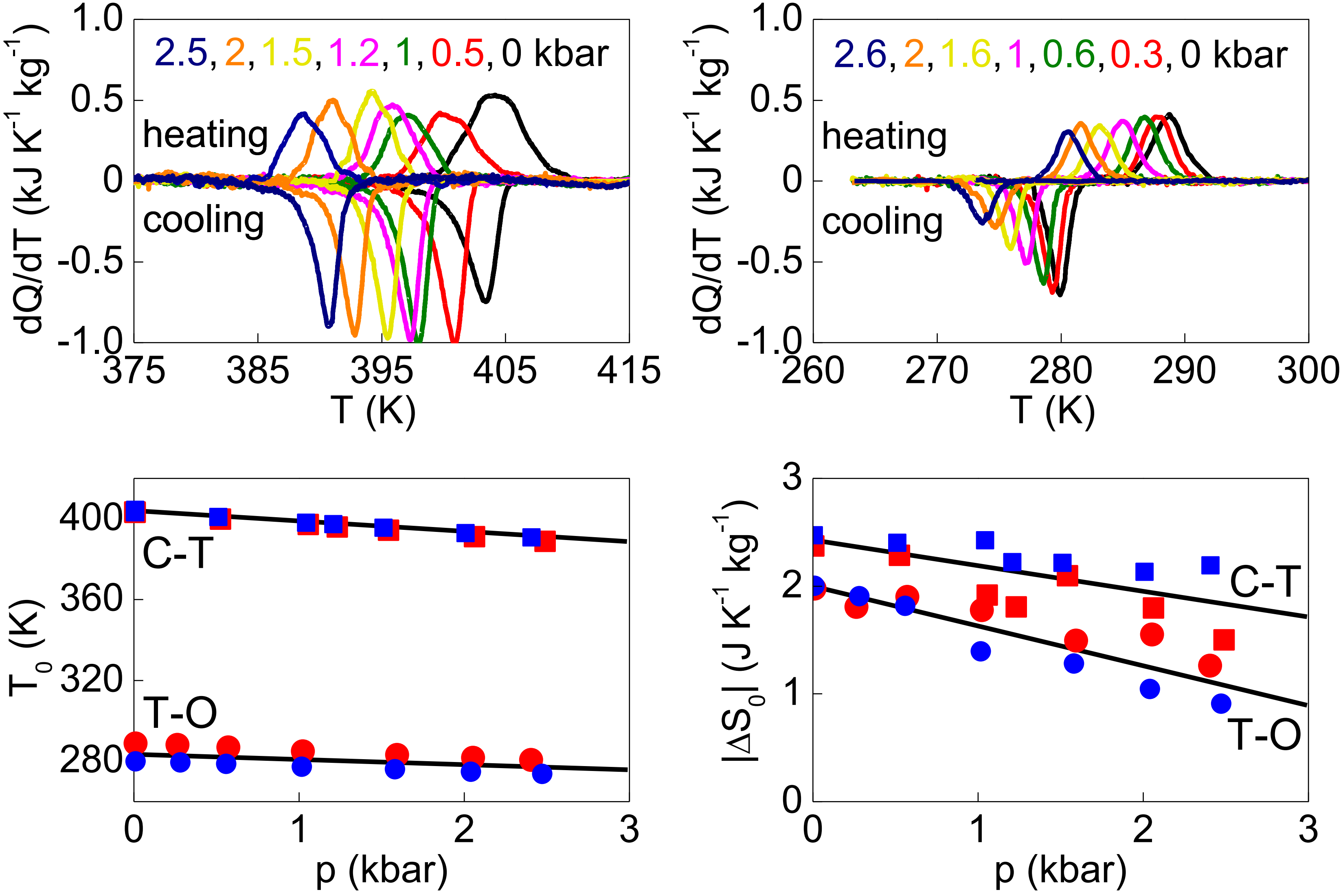
Maxwell relation:

$$\Delta S = -m^{-1}\int_{p_1}^{p_2}\left(\partial V/\partial T\right)_{p'}\mathrm{d}p'$$

$\Delta S > 0$ at transitions

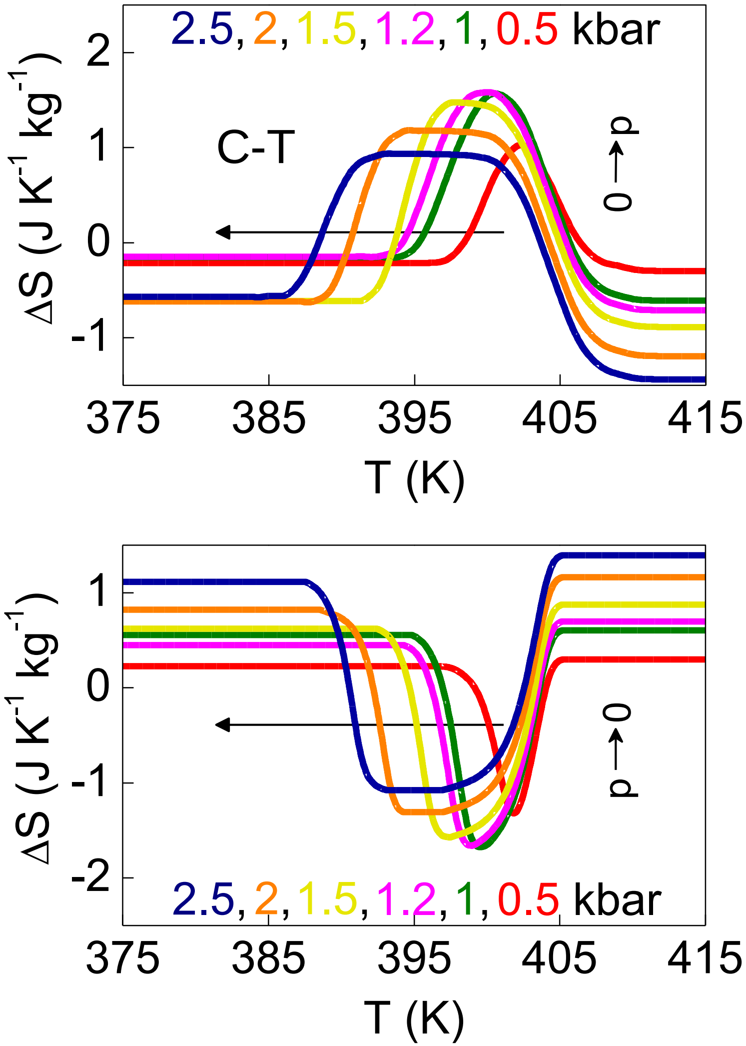
$\Delta S < 0$ elsewhere

Ferroelectric transitions under applied pressure

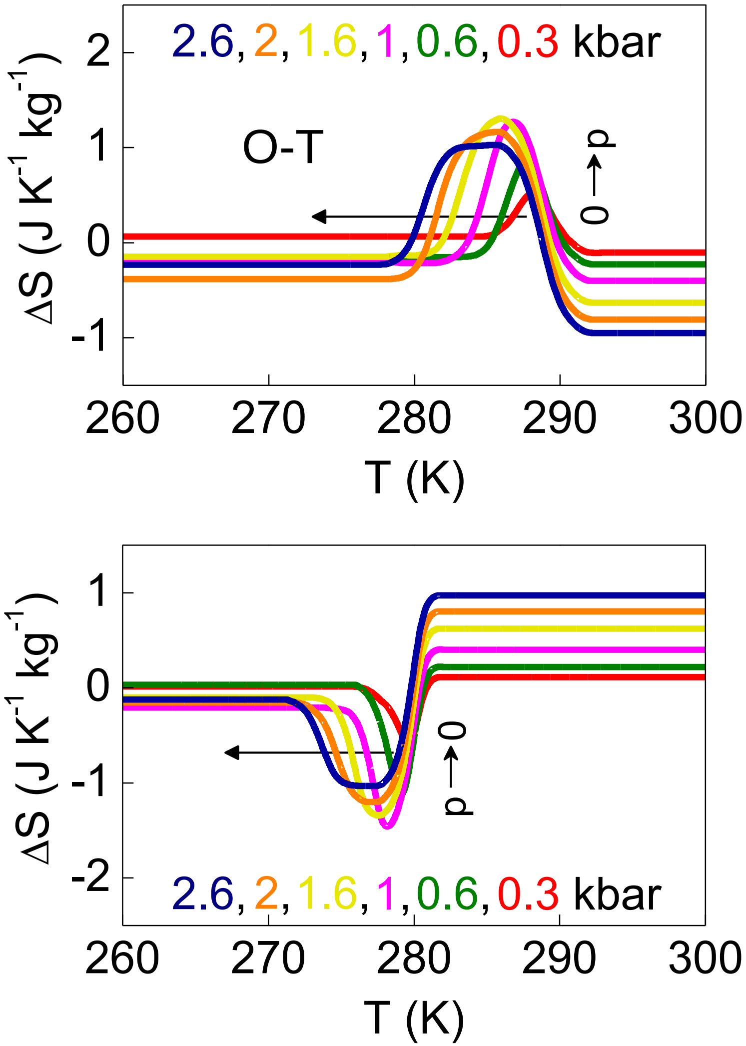


Barocaloric effects in $BaTiO_3$

calorimetry + *V*(*T*)



Highly reversible



Highly irreversible

Caloric effects in $BaTiO_3$

cubic-tetragonal transition

T (K)	Caloric effect	Sample	$\lvert\Delta S_0\rvert$ ($J\ K^{-1}\ kg^{-1}$)	ΔS ($J\ K^{-1}\ kg^{-1}$)	Applied field	Reference
400	**BC**	pc	2.4 ± 0.2	**1.7 ± 0.2**	0.1 GPa	Stern-Taulats *et al.* *APL Materials* **4**, 091102 (2016)
	EC	sc	2.2 ± 0.2	**-2.1**	4 kV cm^{-1}	Moya *et al.* *Adv. Mat.* **25**, 1360 (2013)

tetragonal-orthorhombic transition

T (K)	Caloric effect	Sample	$\lvert\Delta S_0\rvert$ ($J\ K^{-1}\ kg^{-1}$)	ΔS ($J\ K^{-1}\ kg^{-1}$)	Applied field	Reference
280	**BC**	pc	2.0 ± 0.2	**1.2 ± 0.2**	0.1 GPa	Stern-Taulats *et al.* *APL Materials* **4**, 091102 (2016)
	EC	sc	2.3	**-2.3**	10 kV cm^{-1}	Bai *et al.* *AIP Adv.* **2**, 22162 (2012)

Giant barocaloric materials

Giant BC material	T K	$\|\Delta S\|$ J K^{-1} kg^{-1}	$\|Q\|$ kJ kg^{-1}	$\|\Delta p\|$ GPa	$\|\Delta S/\Delta p\|$ J K^{-1} kg^{-1} GPa^{-1}	$\|Q/\Delta p\|$ kJ kg^{-1} GPa^{-1}	Reference
Ni-Mn-In	293	24	7.1	0.26	92.3	27.3	1
$Gd_5Si_2Ge_2$	270	11	2.9	0.20	55	14.5	2
La-Fe-Co-Si	237	8.7	2.0	0.20	43.5	10	3
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Mn_3GaN	285	21.6	6.2	0.09	232	66.2	5
$BaTiO_3$	**400**	**1.7**	**0.7**	**0.10**	**17**	**7**	**6**

[1] Mañosa *et al.*, *Nat. Mater.* **9**, 478 (2010)

[2] Yuce *et al.*, APL **101**, 071906 (2012)

[3] Mañosa *et al.*, *Nat. Commun.* **2**, 592 (2011)

[4] Stern-Taulats *et al.*, PRB **89**, 214105 (2014)

[5] Matsunami *et al.*, *Nat. Mater.* **14**, 73 (2014)

[6] Stern-Taulats *et* al., APL *Materials* **4**, 091102 (2016)

Oxide multicalorics

Background

Brief history of calorics

Thermodynamics and measurements

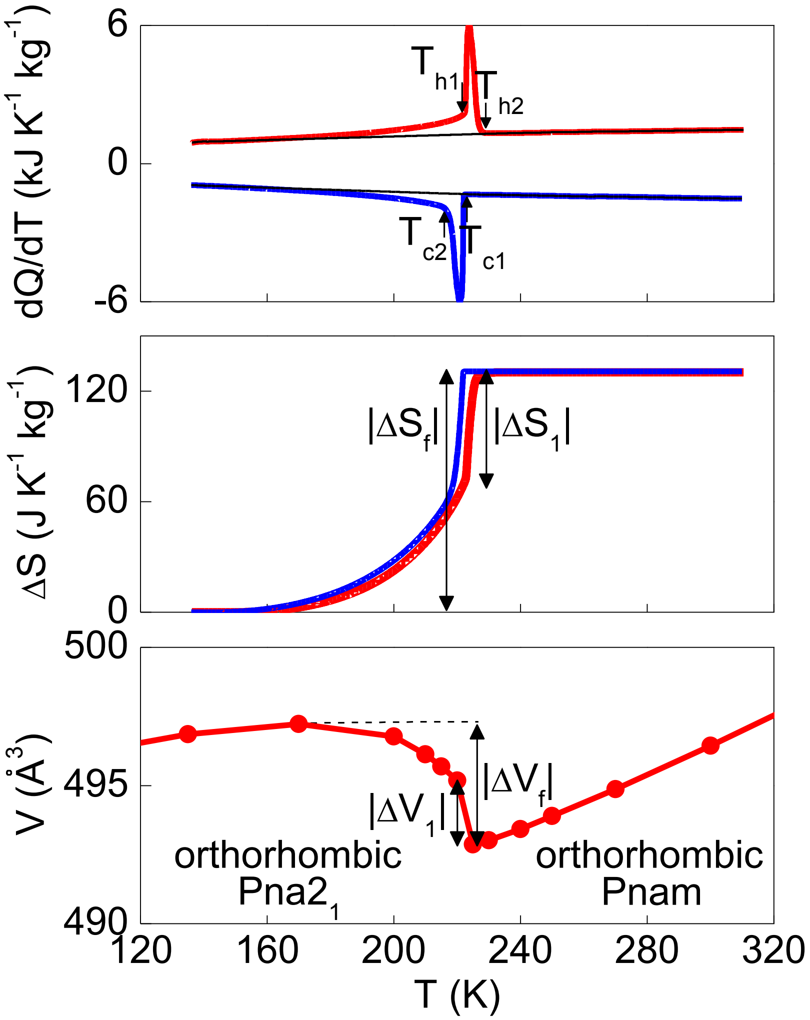
Multicaloric $BaTiO_3$

Multicaloric $(NH_4)_2SO_4$

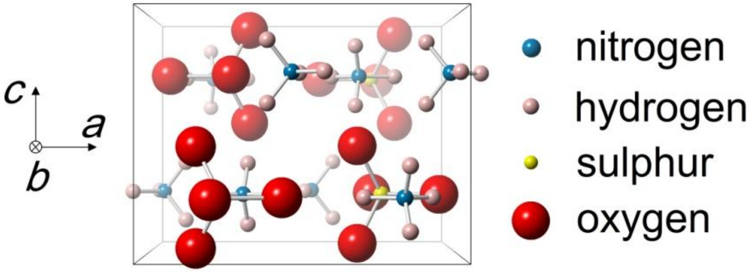
Colossal barocaloric plastic crystals

Ferrielectric phase transition in $(NH_4)_2SO_4$

Thermally driven two-step order-disorder transition

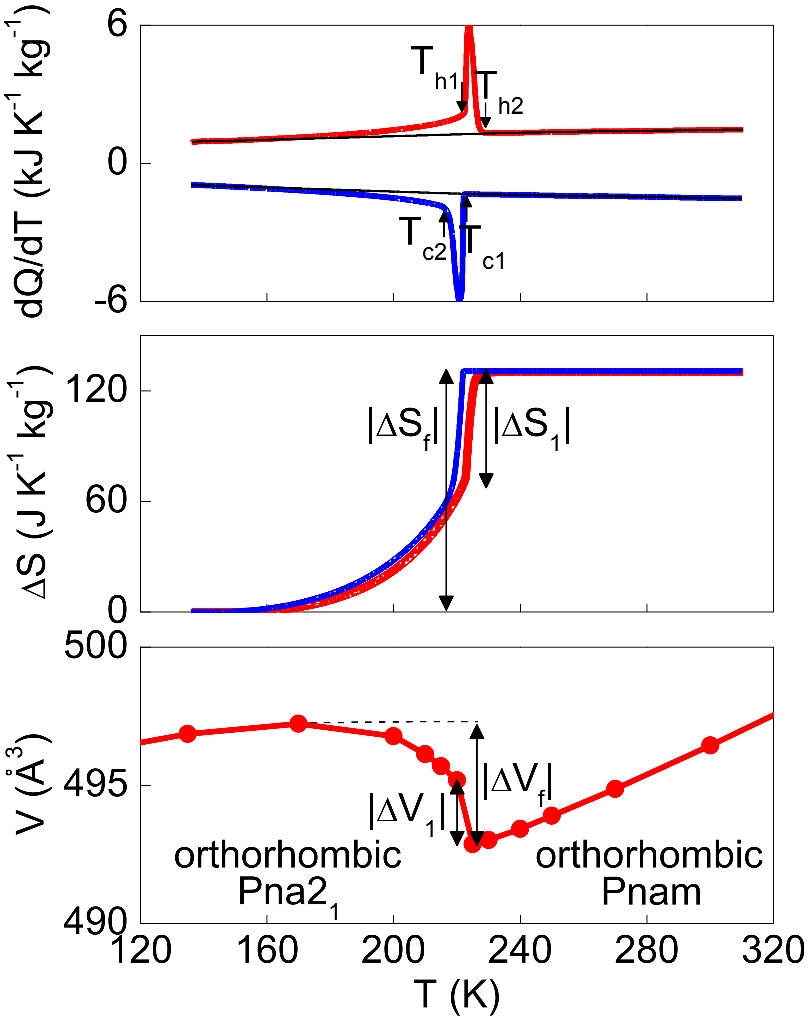


Made of cheap abundant elements



Ferrielectric phase transition in $(NH_4)_2SO_4$

Thermally driven two-step order-disorder transition



Made of cheap abundant elements

Large changes in entropy

$|\Delta S_f| = 130$ J K^{-1} kg^{-1} (= $3R\ln 2$)

$|\Delta S_1| = 65$ J K^{-1} kg^{-1}

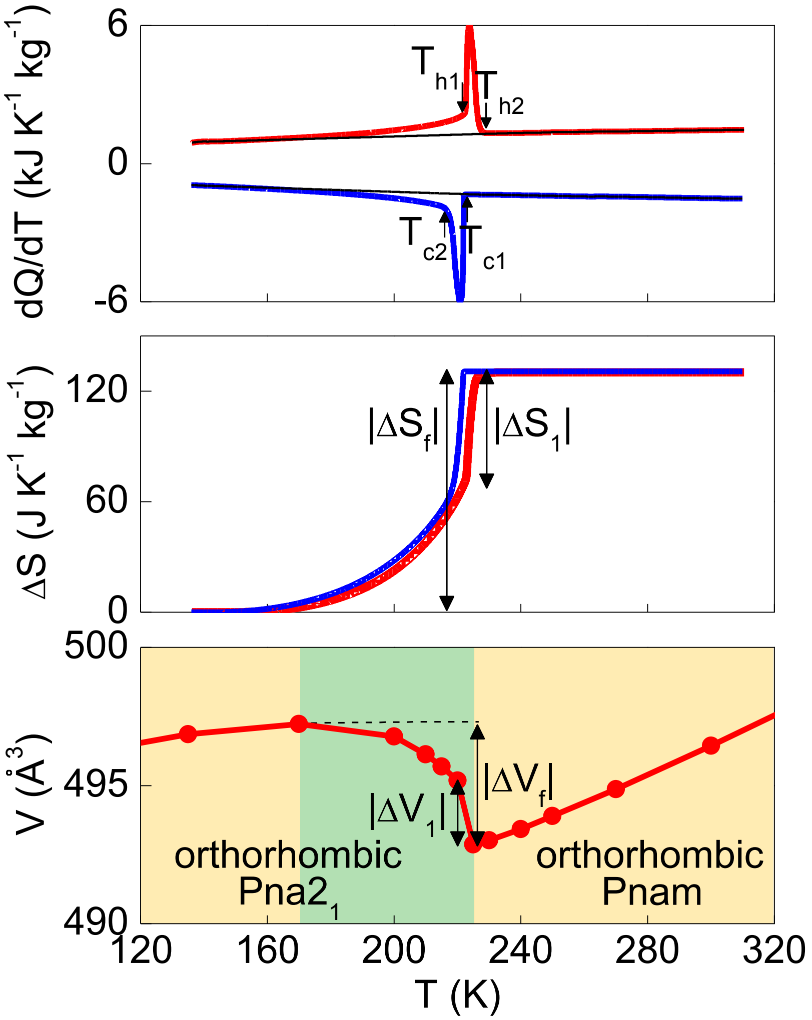
Large changes in volume

$|\Delta V_f|/V_f = 0.9\%$

$|\Delta V_1|/V_1 = 0.5\%$

Ferrielectric phase transition in $(NH_4)_2SO_4$

Thermally driven two-step order-disorder transition



Made of cheap abundant elements

Large changes in entropy

$|\Delta S_f| = 130$ J K^{-1} kg^{-1} ($= 3R\ln 2$)

$|\Delta S_1| = 65$ J K^{-1} kg^{-1}

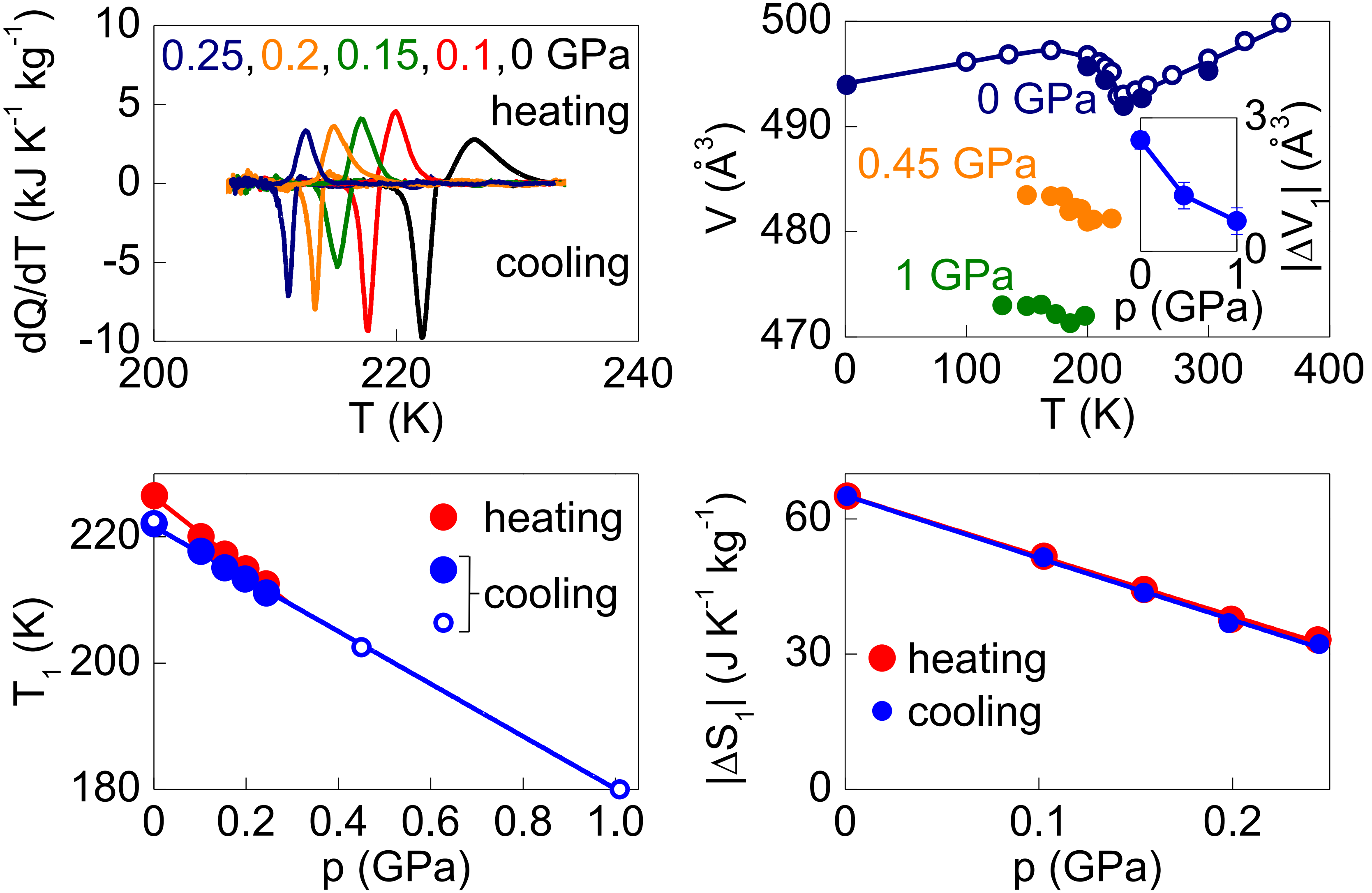
Maxwell relation

$$\Delta S = -m^{-1}\int_{p_1}^{p_2}\left(\partial V/\partial T\right)_{p'}\mathrm{d}p'$$

$\Delta S > 0$ on applying p at transition

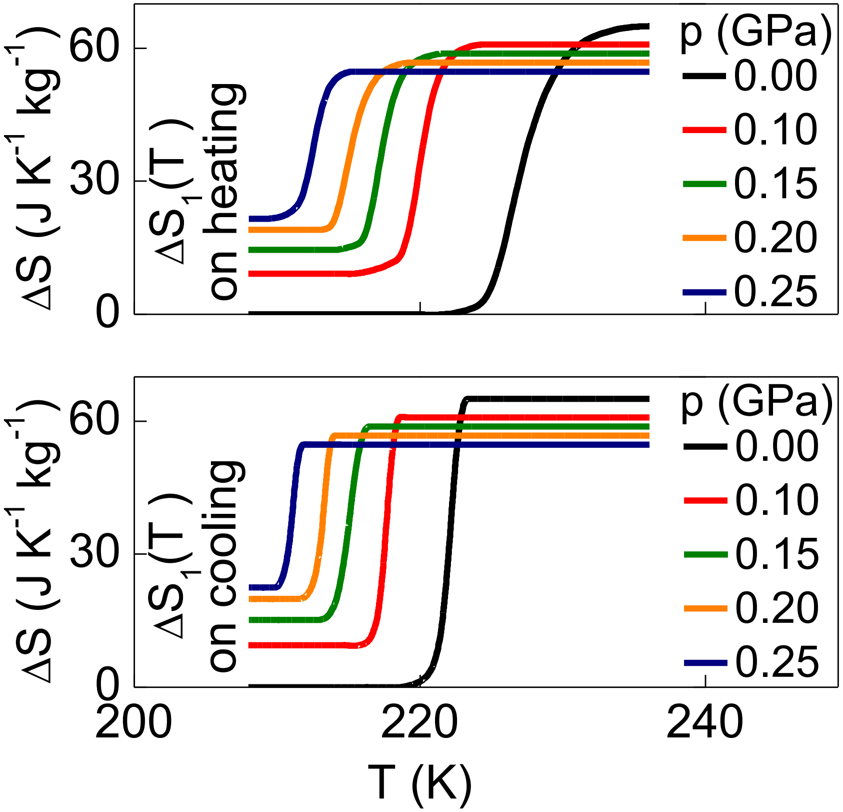
$\Delta S < 0$ on applying p elsewhere

Ferrielectric transition under applied pressure

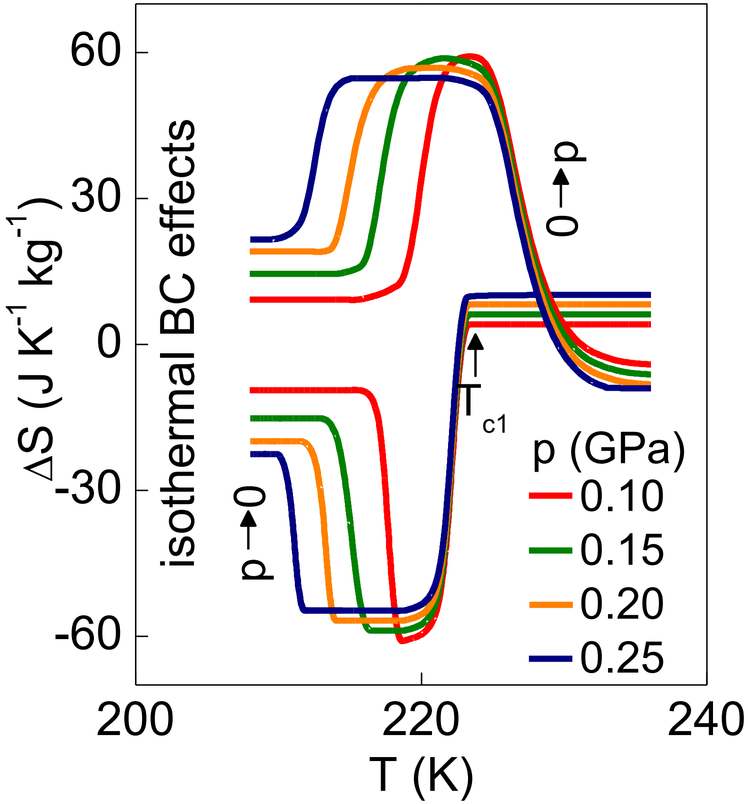


Giant barocaloric effects in $(NH_4)_2SO_4$

calorimetry + *V*(*T*)



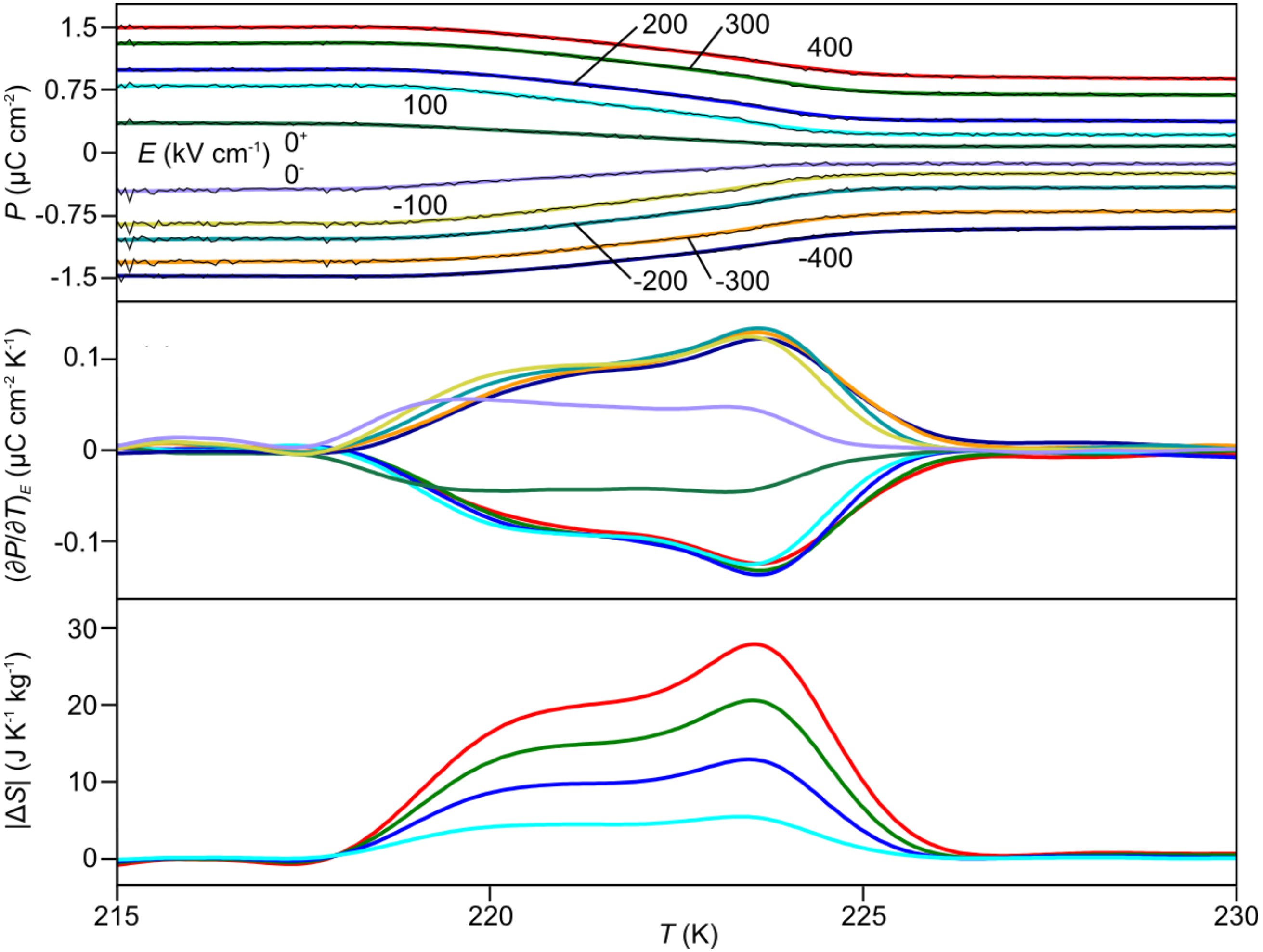
inverse BC effect



Lloveras *et al.*, *Nature Communications* **6**, 8801 (2015)

Giant electrocaloric effects in $(NH_4)_2SO_4$

50 µm-thick single crystal



$$\Delta S = \frac{1}{\rho}\int_0^E \left(\frac{\partial P}{\partial T}\right)_{E'} dE'$$

Crossley *et al.*, *Phil. Trans. R. Soc. A* **374**, 20150313 (2016)

Giant barocaloric materials

Giant BC material	**T** **K**	**$\lvert\Delta S\rvert$** **J K^{-1} kg^{-1}**	**$\lvert Q\rvert$** **kJ kg^{-1}**	**$\lvert\Delta p\rvert$** **GPa**	**$\lvert\Delta S/\Delta p\rvert$** **J K^{-1} kg^{-1} GPa^{-1}**	**$\lvert Q/\Delta p\rvert$** **kJ kg^{-1} GPa^{-1}**	**Reference**
Ni-Mn-In	293	24	7.1	0.26	92.3	27.3	1
$Gd_5Si_2Ge_2$	270	11	2.9	0.20	55	14.5	2
La-Fe-Co-Si	237	8.7	2.0	0.20	43.5	10	3
$Fe_{49}Rh_{51}$	308	12.5	3.8	0.11	114	34.5	4
Mn_3GaN	285	21.6	6.2	0.09	232	66.2	5
$BaTiO_3$	**400**	**1.7**	**0.7**	**0.10**	**17**	**7**	**6**
$(NH_4)_2SO_4$	**219**	**60**	**13.2**	**0.10**	**600**	**132**	**7**

[1] Mañosa *et al.*, *Nat. Mater.* **9**, 478 (2010)
[2] Yuce *et al.*, APL **101**, 071906 (2012)
[3] Mañosa *et al.*, *Nat. Commun.* **2**, 592 (2011)
[4] Stern-Taulats *et al.*, PRB **89**, 214105 (2014)
[5] Matsunami *et al.*, *Nat. Mater.* **14**, 73 (2014)
[6] Stern-Taulats *et* al., APL *Materials* **4**, 091102 (2016)
[7] Lloveras *et al.*, *Nat. Commun.* **6**, 8801 (2015)

Oxide multicalorics

Background

Brief history of calorics

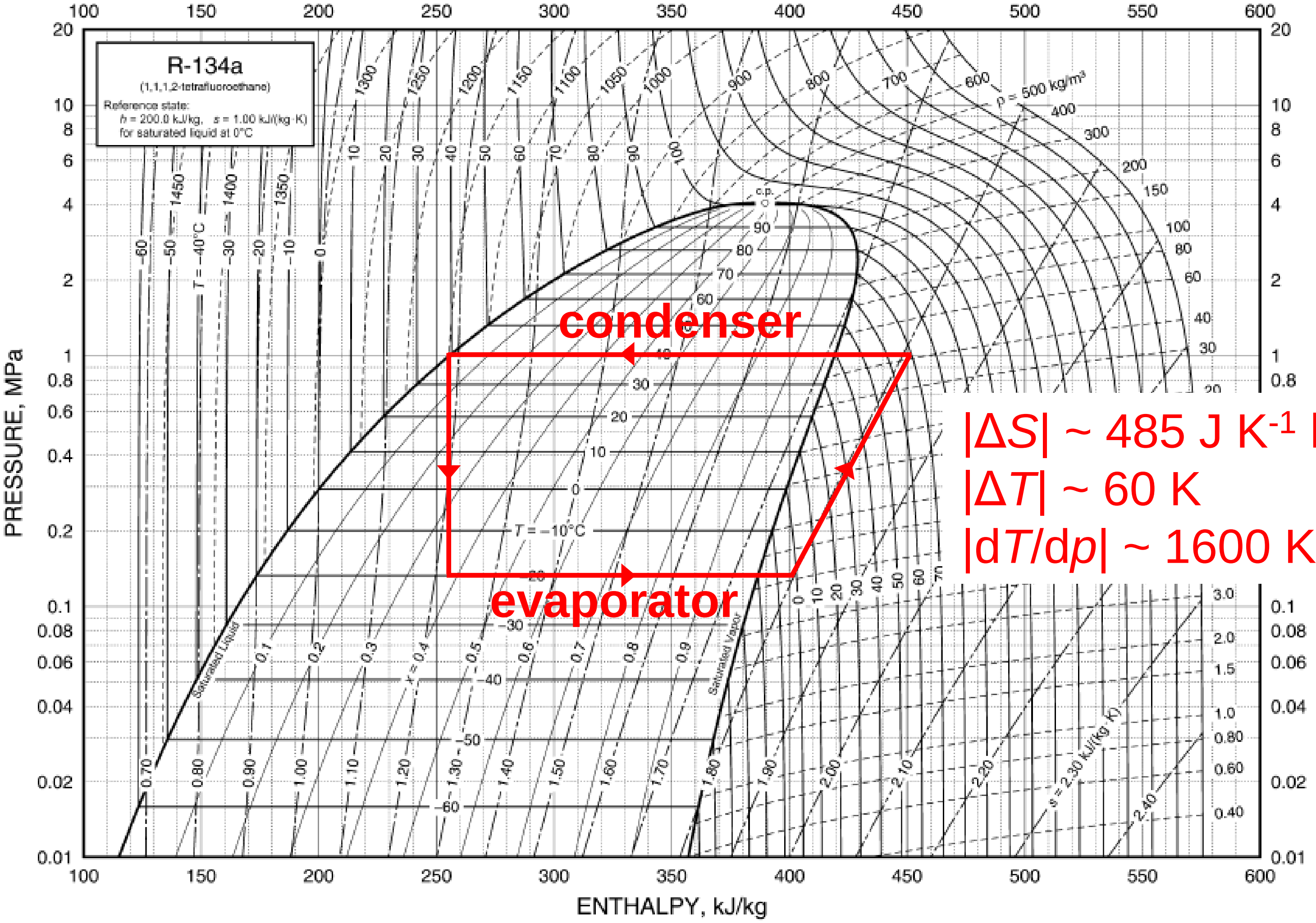
Thermodynamics and measurements

Multicaloric $BaTiO_3$

Multicaloric $(NH_4)_2SO_4$

Colossal barocaloric plastic crystals

The challenge



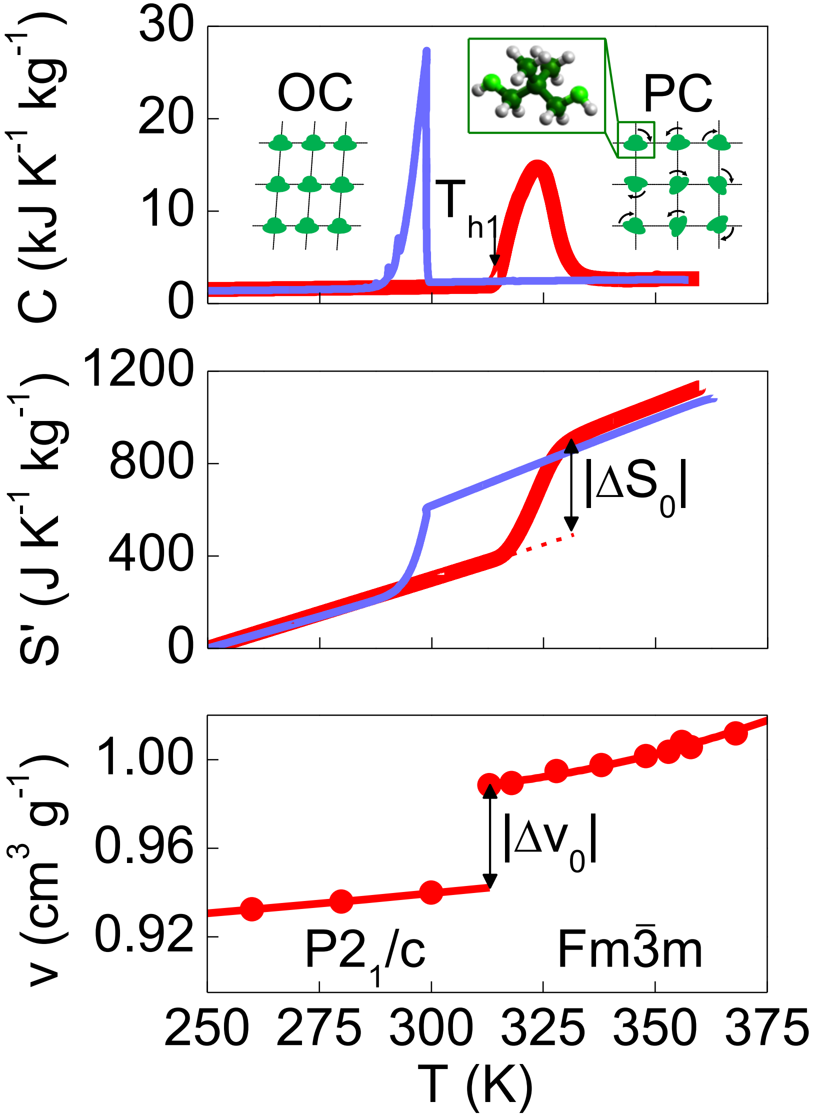
$|\Delta S| \sim 485\ \mathrm{J\ K^{-1}\ kg^{-1}}$

$|\Delta T| \sim 60\ \mathrm{K}$

$|\mathrm{d}T/\mathrm{d}p| \sim 1600\ \mathrm{K\ GPa^{-1}}$

ASHRAE (2013)

Orientational phase transition in neopentylglycol



Made of cheap abundant elements

$(CH_3)_2C(CH_2OH)_2$

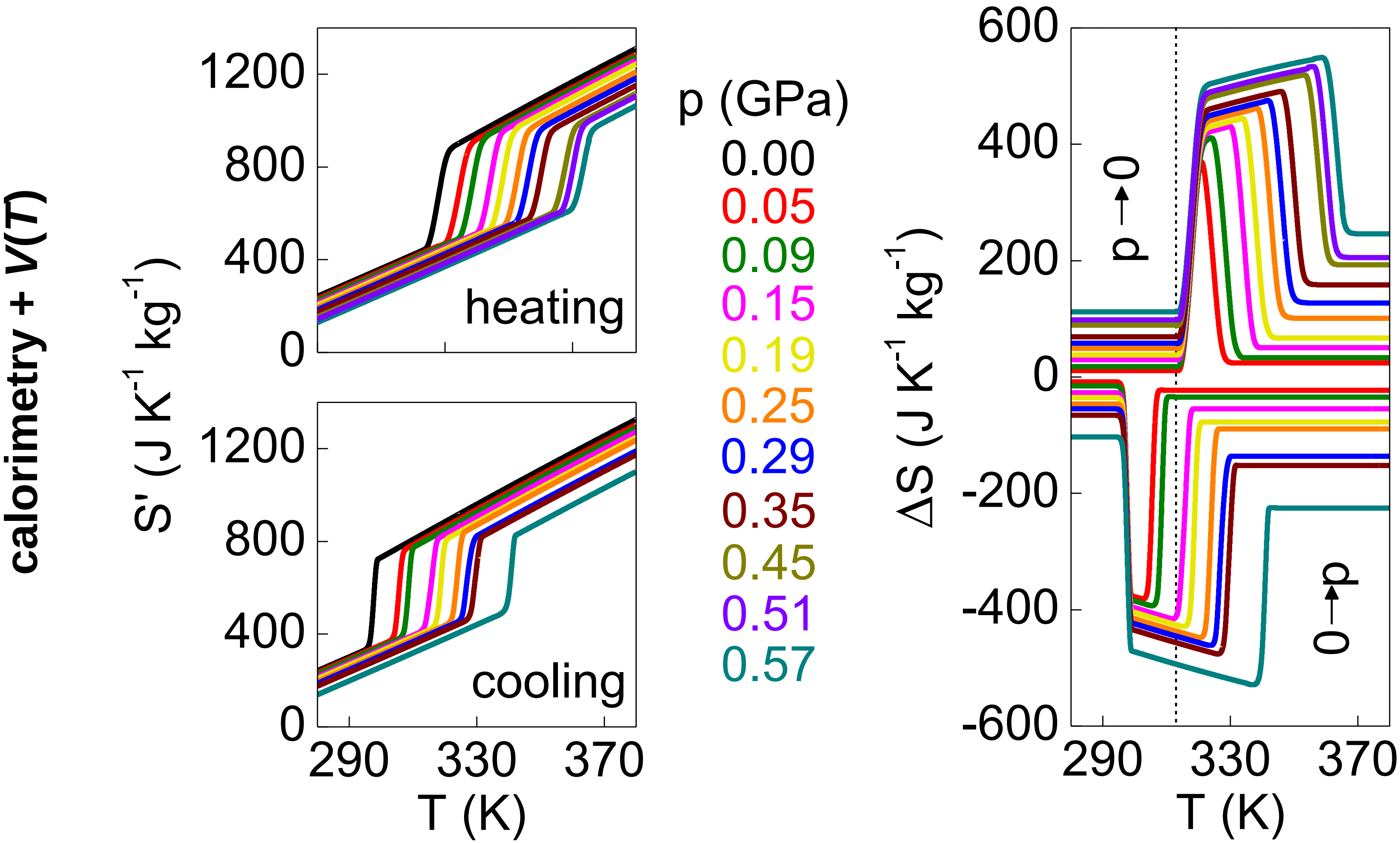
Large changes in entropy

$|\Delta S_0|$ = 380 J K^{-1} kg^{-1}

Large changes in volume

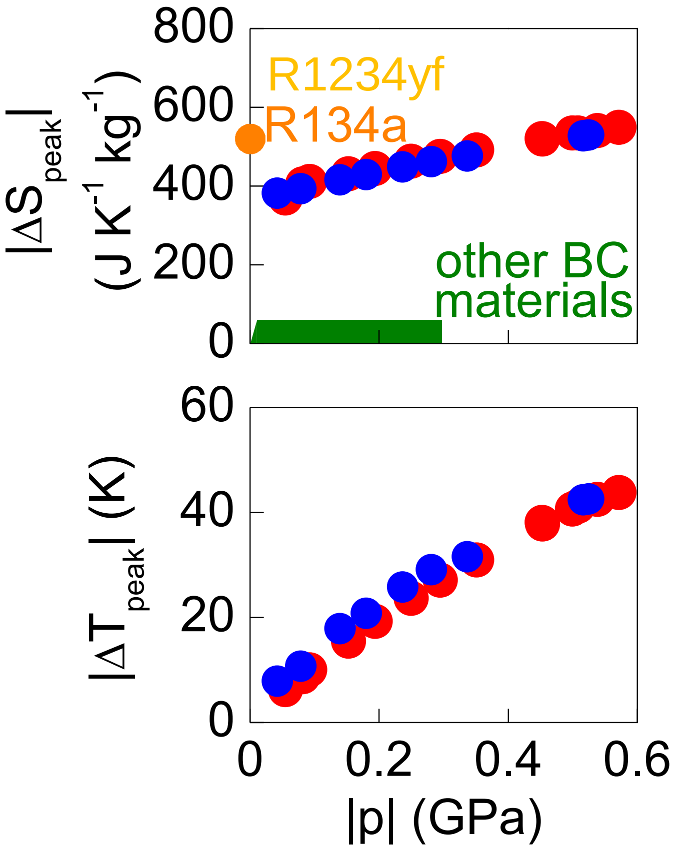
$|\Delta V_0|/V_0$= 4.9%

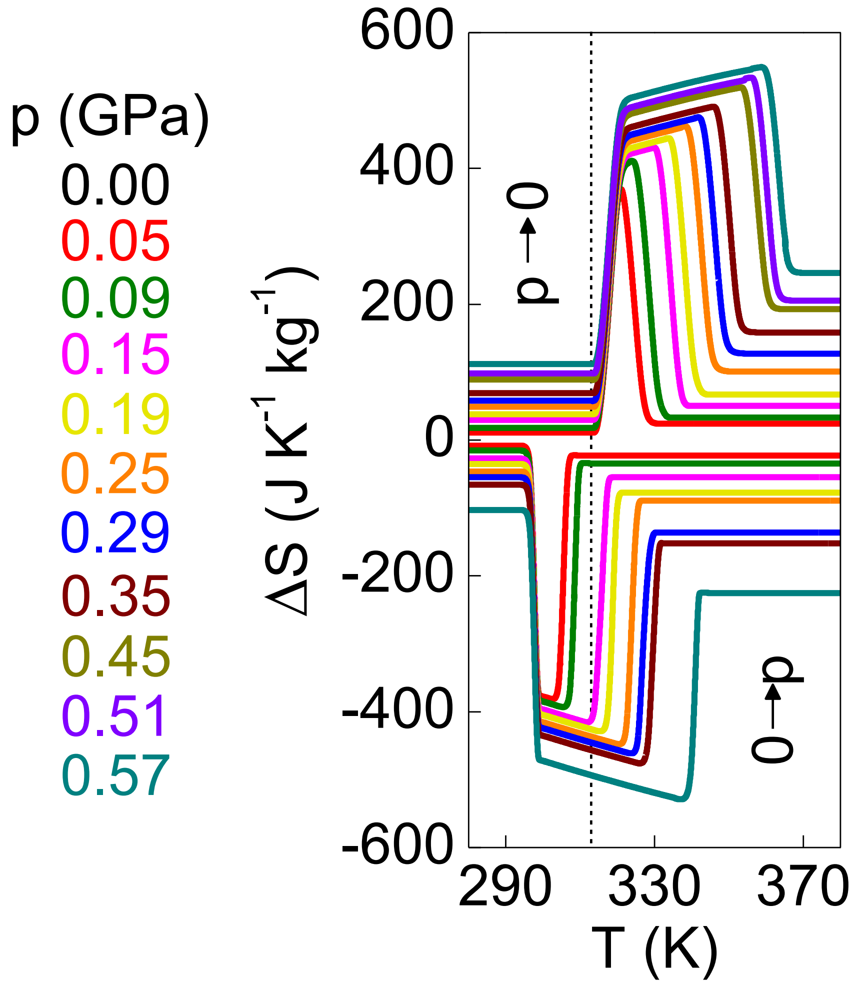
Colossal barocaloric effects in neopentylglycol



Lloveras *et al.*, *Nature Communications* **10**, 1803 (2019)

Colossal barocaloric effects in neopentylglycol



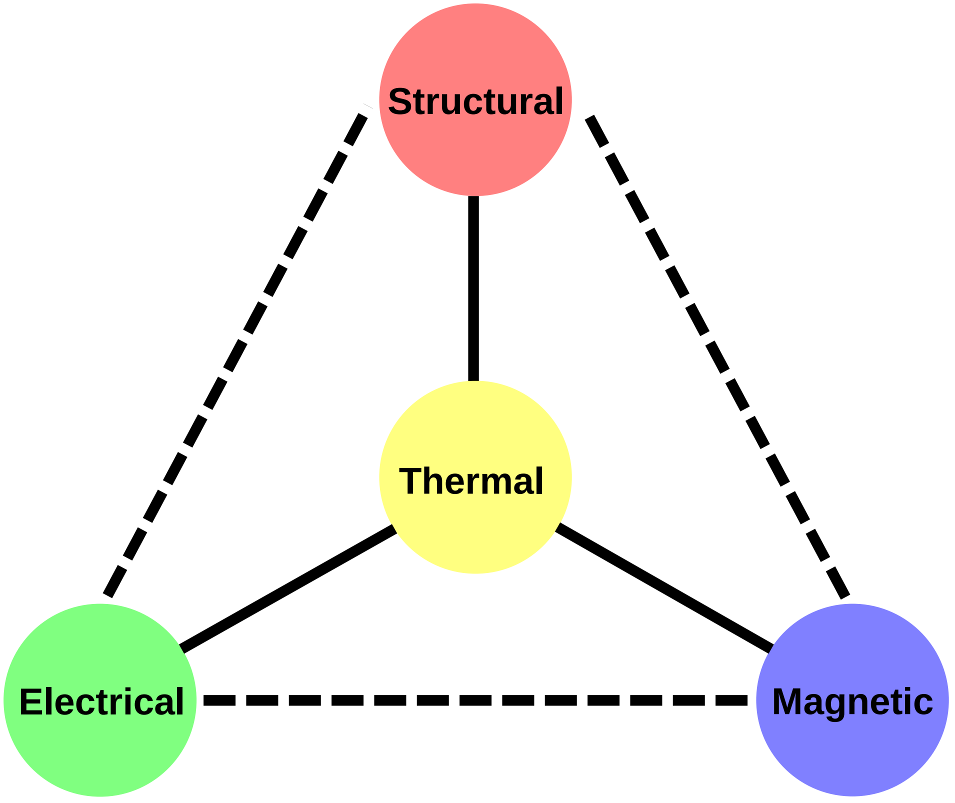


Patent GB1617508.5 (2016)
PCT/EP2017/076203 (2017)
WO2018/069506 (2018)

Lloveras *et al.*, *Nature Communications* **10**, 1803 (2019)

Oxide multicalorics

Extremely fertile playground for calorics



The Times They Are A-Changin'

Bob Dylan, 1964