Pressure-induced phase transitions for solid-state cooling: Barocaloric effect

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Group of Characterization of Materials

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Araceli Aznar
Vapor compression refrigeration cycle

Needed everywhere

Buildings: Homes, offices

Transport

Industry

Data centers, web servers

Storage of food, medicines, vaccines, blood, artwork

- 1914: First domestic air-conditioning unit
- 1930: First domestic fridge
- 2010: 50 000 000 units sold in China in 2010
- 2014: Cooling > 20% world-electricity consumption
- Future: Growth > 30-fold from 2000 to 2100
Vapor compression refrigeration cycle

**Drawback: Leakage of harmful refrigerant fluids**

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- Long piping (up to hundreds of m in domestic units)
- Large amounts of refrigerant required (up to 50 kg)
- Installation often made by end users
- Mandatory leak inspections are often unfeasible
- Costly waste management

- In Germany, stationary air conditioning units caused 717400 tons CO₂ equivalent
- 60% of world HFC emissions arise from leaks
- 2050: Almost 10% of global greenhouse gas emissions
Vapor compression refrigeration cycle

Ex: Reverse Brayton cycle: adiabatic + isobaric processes

Pressure $p$ – Volume $v$

Entropy $S$ – Temperature $T$

$p$ – Volume $v$

Entropy $S$ – Temperature $T$

$S_2 (< S_1)$

$S_1$

$T_1 (> T_2)$

$T_2 (> T_3)$

$T_3$

$p_1$

$S(T)_{p_1}$

$S(T)_{p_2}$

$T_2$
Vapor compression refrigeration cycle

Ex: Reverse Brayton cycle: adiabatic + isobaric processes

Pressure $p$ – Volume $v$

Entropy $S$ – Temperature $T$

$S_2 (< S_1)$

+$Q$

$T_1 (> T_2)$

$T_2 (> T_3)$

$T_3$

$S(T)_{p_1}$

$S(T)_{p_2}$
Vapor compression refrigeration cycle
Ex: Reverse Brayton cycle: adiabatic + isobaric processes

Pressure $p$ – Volume $v$

Entropy $S$ – Temperature $T$

$p_1$ $p_2$

$S_1$ $S_2 (< S_1)$

$T_1 (> T_2)$ $T_2 (> T_3)$ $T_3$

$-Q$

$S(T)_{p_1}$ $S(T)_{p_2}$

$T_3$ $T_2$ $T_1$
Vapor compression refrigeration cycle

Ex: Reverse Brayton cycle: adiabatic + isobaric processes

Pressure $p$ – Volume $v$

Entrophy $S$ – Temperature $T$
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Ex: Reverse Brayton cycle: adiabatic + isobaric processes

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Entropy $S$ – Temperature $T$
Vapor compression refrigeration cycle

**Ex: Reverse Brayton cycle: adiabatic + isobaric processes**

Pressure $p$ – Volume $v$

Entropy $S$ – Temperature $T$

**Barocaloric effects:**
- **Adiabatic $\Delta T$**
- **Isothermal $\Delta S$**

Upon application of pressure
Barocaloric effects

Upon application of pressure

Adiabatic $\Delta T$

 Isothermal $\Delta S$

 Isothermal $dT = 0$

 Adiabatic (rev.) $dS = 0$

$TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_T dp$

$\Delta S_{isot} (T, \Delta p) = - \int_{p_I}^{p_F} \left( \frac{\partial V}{\partial T} \right)_p dp$

$\Delta T_{ad} (T, \Delta p) = \int_{p_I}^{p_F} \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_p dp$

Entropy $S$

Temperature $T$
Barocaloric effects

\[ \text{Adiabatic } \Delta T \]
\[ \text{Isothermal } \Delta S \]

\[ \text{Upon application of pressure} \]

Isothermal

\[ dT = 0 \]

\[ TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_T dp \]

Adiabatic (rev.)

\[ dS = 0 \]

\[ \Delta S_{\text{isot}} (T, \Delta p) = -\int_{p_1}^{p_F} \left( \frac{\partial V}{\partial T} \right)_p dp \]

\[ \Delta T_{\text{ad}} (T, \Delta p) = \int_{p_1}^{p_F} \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_p dp \]
Barocaloric effects

 Upon application of pressure

 Isothermal $\Delta S$

 Adiabatic $\Delta T$

 Isothermal $dT = 0$

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 $\Delta S_{\text{isot}} (T, \Delta p) = -\int_{p_1}^{p_F} \left( \frac{\partial V}{\partial T} \right)_p dp$

 $\Delta T_{\text{ad}} (T, \Delta p) = \int_{p_1}^{p_F} \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_p dp$

 $\sim$ Thermal expansion: large for gases

 Vapor compression refrigeration cycle

 $TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_T dp$
Barocaloric effects

Upon application of pressure

\[\Delta T \quad \text{Adiabatic} \]
\[\Delta S \quad \text{Isothermal} \]

\( TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_T dp \)

\( \Delta S_{\text{isot}}(T, \Delta p) = - \int_{p_1}^{p_f} \left( \frac{\partial V}{\partial T} \right)_p dp \)

\( \Delta T_{\text{ad}}(T, \Delta p) = \int_{p_1}^{p_f} \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_p dp \)

\(~ \text{Thermal expansion: large for gases} ~\)

Vapor compression refrigeration cycle

May be large for solids at first-order phase transitions

\(~ \text{large for gases} ~\)
Barocaloric effects

\[ \text{Adiabatic } \Delta T \quad \text{ upon application of pressure} \]
\[ \text{Isothermal } \Delta S \]

\[ TdS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_T \]
\[ dS = 0 \quad \text{ Adiabatic (rev.)} \]

\[ \Delta S_{\text{isot}} (T, \Delta p) = - \int_{p_1}^{p_f} \left( \frac{\partial V}{\partial T} \right)_p dp \]

\[ \Delta T_{\text{ad}} (T, \Delta p) = \int_{p_1}^{p_f} \frac{T}{C_p} \left( \frac{\partial V}{\partial T} \right)_p dp \]

\sim \text{ Thermal expansion: large for gases}

\sim \text{ Thermal expansion: large for solids at first-order phase transitions}

\sim \text{ Vapor compression refrigeration cycle}

\sim \text{ Solid-state barocaloric effects:}
- Overcomes problems of leakage
- Offers more compact devices
- Fast response
- Efficiency?
Solid-solid first-order phase transitions: Clausius-Clapeyron

\[ \frac{dT}{dp} = \frac{\Delta V_t}{\Delta S_t} \]

\[ \Delta V_t(T_1, p_1) \]

\[ \Delta S_t(T_1, p_1) \]
Solid-solid first-order phase transitions: Clausius-Clapeyron

\[
\frac{dT}{dp} = \frac{\Delta V_t}{\Delta S_t}
\]

\[
\Delta V_t(T_1, p_1)
\]

\[
\Delta V_t(T_2, p_2)
\]

\[
\Delta S_t(T_1, p_1)
\]

\[
\Delta S_t(T_2, p_2)
\]
Solid-state barocaloric refrigeration cycle

Ex: Reverse Brayton cycle
Solid-state barocaloric refrigeration cycle

Ex: Reverse Brayton cycle

- Entropy $S$
- Temperature $T$

$S(T)_{p_I}$

$S(T)_{p_F}$

Entropy vs. Temperature graph

Solid-state barocaloric refrigeration cycle diagram
Solid-state barocaloric refrigeration cycle

Ex: Reverse Brayton cycle
Solid-state barocaloric refrigeration cycle

Ex: Reverse Brayton cycle
Solid-state barocaloric refrigeration cycle

Ex: Reverse Brayton cycle
Calculation of isobaric entropy curves: Quasi-direct method

High-pressure calorimetry (DSC-DTA)

\[ S(T, p) = \int \frac{1}{T} \frac{dq(p)}{dT} dT \]

\[ C_p \]

\[ \Delta S = S(T, 0) - S(300, 0) \]

\[ T(K) \]

\[ \Delta S_{240} \]

\[ T(K) \]
Calculation of isobaric entropy curves: Quasi-direct method

High-pressure calorimetry (DSC-DTA)

\[ S(T, p) = \int \frac{1}{T} \frac{dq(p)}{dT} dT \]

\[ S - S_{240K} \text{ (J K}^{-1} \text{ kg}^{-1}) \]

\[ \int dT(dq(T)) \]

\[ C_p \]

\[ L \]

0 GPa

0.35 GPa
Calculation of isobaric entropy curves: Quasi-direct method

High-pressure calorimetry (DSC-DTA)

\[
S(T, p) = \int \frac{1}{T} \frac{dq(p)}{dT} \, dT
\]

\[
\Delta S(T, p_{atm} \rightarrow p) = -\int_{p_{atm}}^{p} \left( \frac{\partial V}{\partial T} \right)_p \, dp
\]
Calculation of barocaloric effects: Quasi-direct method

\[ S - S_{240K} \ (J K^{-1} \ kg^{-1}) \]

\[ \Delta S \]

\[ \Delta T \]

0 GPa

0.35 GPa
Calculation of barocaloric effects: Quasi-direct method

Isothermal entropy changes

0.35 GPa $\rightarrow$ 0

Adiabatic temperature changes

0.35 GPa $\rightarrow$ 0

\[
\Delta S = \frac{\partial S}{\partial T} \Delta T
\]

\[
S - S_{240\text{K}} (\text{J K}^{-1} \text{kg}^{-1})
\]

0 GPa

0.35 GPa
Calculation of barocaloric effects: Clausius-Clapeyron

High-pressure calorimetry

Transition entropy change

$|\Delta S| (\text{J K}^{-1} \text{kg}^{-1})$

$\frac{dT}{dp}$

$T-p$ Phase diagram

Calculation of barocaloric effects: Clausius-Clapeyron
Calculation of barocaloric effects: Clausius-Clapeyron

High-pressure calorimetry

Transition entropy change

$\Delta S$ (J K$^{-1}$ kg$^{-1}$)

$p$ (GPa)

$T$ (K)

$|\Delta v|$ (cm$^3$ g$^{-1}$)

$\Delta v = \frac{dT}{dp} \Delta S$

$T$-$p$ Phase diagram

Transition volume change

$\frac{dT}{dp}$

$\Delta v$ (cm$^3$ g$^{-1}$)

$p$ (GPa)
Calculation of barocaloric effects: Clausius-Clapeyron

High-pressure calorimetry

Conventional X-ray diffraction

Transition entropy change

$\Delta S_t$ (J K$^{-1}$ kg$^{-1}$)

$T$ (K)

$T$-$p$ Phase diagram

Transition volume change

$\Delta V_t$ (cm$^3$ g$^{-1}$)

$\Delta v = \frac{dT}{dp} \Delta S$

$\frac{dT}{dp}$
Calculation of barocaloric effects: Clausius-Clapeyron

High-pressure calorimetry

Conventional & synchrotron high-pressure X-ray diffraction

Transition entropy change

T-p Phase diagram

Transition volume change

\[ \Delta S = \frac{dT}{dp} \Delta S \]
Calculation of barocaloric effects: Clausius-Clapeyron

High-pressure calorimetry

Conventional & synchrotron high-pressure X-ray diffraction

Dilatometry

Transition entropy change

T-p Phase diagram

Transition volume change

\[ \Delta S = \frac{dT}{dp} \]

\[ \Delta V = \frac{dT}{dp} \Delta S \]
Giant barocaloric materials
General requirements of competitive candidates

· First-order solid-state transition involving large latent heat and volume changes
· Small hysteresis to enhance reversibility
· Appropriate temperature regimes
· Cyclability (no breakdown, no fatigue)
· High thermal conductivity to enhance heat transfer
· Cheap, abundant, non-toxic
· High density for more compact devices
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

Ordering of spins

![Graph showing the relationship between pressure (p) and peak entropy change (|ΔS_{peak}|) for different materials.](image-url)
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

Ordering of spins

Emergence of net polarization

Emergence of net polarization

\[ \Delta S_{\text{peak}} \text{ (J K}^{-1} \text{ kg}^{-1}) \]

Materials:
- MnNiSi-FeCoGe
- (NH\(_4\))\(_2\)SO\(_4\)
- MnCoGeIn
- NiMnIn
- NiCoMnGaIn
- GdSiGe
- LaFeCoSi
- MnGaN
- FeRh
- BaTiO\(_3\)
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

- Superionic transitions
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

- Superionic transitions

- Fluoride salts
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

- Superionic transitions

- Fluoride salts
- Hybrid organic-inorganic compounds: Metalorganic frameworks
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions
  - Ordering of spins

- Ferroelectric transitions
  - Emergence of net polarization

- Superionic transitions
  - Melting of sublattice

- Fluoride salts
- Hybrid organic-inorganic compounds:
  Metalorganic frameworks
- Polymers: Natural Rubber, PVDF…
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

- Superionic transitions

- Orientationally Disordered Crystals

- Fluoride salts
- Hybrid organic-inorganic compounds: Metalorganic frameworks
- Polymers: Natural Rubber, PVDF…
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

- Superionic transitions

- Orientationally Disordered Crystals

- Fluoride salts
- Hybrid organic-inorganic compounds: Metalorganic frameworks
- Polymers: Natural Rubber, PVDF…
Caloric effects: Generalization in Ferroic and multiferroic systems

Barocaloric
$X$: Volume $V$
$Y$: Pressure $-p$

Elastocaloric
$X$: Strain, $\varepsilon$
$Y$: uniaxial stress, $\sigma$

Magnetocaloric
$X$: Magnetization, $M$
$Y$: Magnetic Field, $H$

Electrocaloric
$X$: Polarization, $P$
$Y$: Electric Field, $E$

- Pressure: easy to generate
- Powder $\rightarrow$ no fatigue
- Very large effect
- Plastic deformation and fatigue: Loss and mechanical breakdown
- High efficiency, quiet
- First prototypes
- Large magnetic Fields required: Expensive and difficult to generate
- Toxic or expensive materials
- Thin films: Very large effects
- Need of fabrication of multilayers
- Bulk materials: Low breakdown fields
Solid-state magnetocaloric refrigeration cycle

Ex: Reverse Brayton cycle

Entropy $S$

Temperature $T$

$S(T)_{H_f}$

$S(T)_{H_f}$

+Q

-Q

$-[Q] + [Q]$
Solid-state magnetocaloric refrigeration cycle

Ex: Reverse Brayton cycle
Multicaloric strategies


Enhancement of caloric magnitudes & temperature shift

La Fe$_{11.6}$Si$_{1.4}$

Morellon et al., PRL 93, 137201 (2004)

Tb$_5$Si$_2$Ge$_2$

Liu et al., Nature Mater. 11, 620 (2012)

Magnetic entropy change, $\Delta S_M (J / kg-K)$

Reduction of the effective hysteresis
Solid-state caloric and multicaloric effects may offer an alternative to current compression methods that use harmful gases.

Additional advantages may be higher efficiencies, more compact devices and faster responses, as demonstrated by the existing prototypes.

There is a need of finding materials meeting the requirements for a competitive implementation.
Hysteresis losses in caloric effects
Hysteresis losses in caloric effects

![Graph showing hysteresis losses in caloric effects with axes labeled as follows: T (K) on the y-axis and p (kbar) on the x-axis. The graph includes lines for heating and cooling, with specific temperature and pressure ranges indicated.]
Hysteresis losses in caloric effects
Consequences of hysteresis losses on caloric effects

![Graph showing the effects of hysteresis losses on caloric effects.](image)
Consequences of hysteresis losses on caloric effects

\[ \Delta S \quad (\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}) \]

\[ T \quad (\text{K}) \]

\[ p \rightarrow 0 \]

\[ \Delta T \quad (\text{K}) \]

\[ p \rightarrow 0 \]
Consequences of hysteresis losses on caloric effects

\[ \Delta S \left( \text{J K}^{-1} \text{kg}^{-1} \right) \]

\[ T \left( \text{K} \right) \]

\[ \Delta T \left( \text{K} \right) \]

\[ p \to 0 \]
Consequences of hysteresis losses on caloric effects

\[ \Delta S (\text{J/K/kg}) \]

\[ T (\text{K}) \]

\[ \Delta T (\text{K}) \]

\[ 280 \rightarrow p \]
Consequences of hysteresis losses on caloric effects

\[ \Delta S (\text{J K}^{-1} \text{kg}^{-1}) \]

\[ T (\text{K}) \]

\[ \Delta T (\text{K}) \]

\[ p \rightarrow 0 \]

\[ 0 \rightarrow p \]
Consequences of hysteresis losses on caloric effects

\[ \Delta S \text{ (J K}^{-1} \text{kg}^{-1}) \]

\[ T \text{ (K)} \]

\[ \Delta T \text{ (K)} \]

\[ p \to 0 \]

\[ 0 \to p \]
Consequences of hysteresis losses on caloric effects
Calculation of isobaric entropy curves: Quasi-direct method

High-pressure calorimetry (DSC-DTA)

\[ S(T, p) = \int \frac{1}{T} \frac{dq(p)}{dT} \, dT \]

(High-pressure) X-ray diffraction, dilatometry

\[ \Delta S(T, p_{atm} \to p) = -\int_{p_{atm}}^{p} \left( \frac{\partial V}{\partial T} \right)_p \, dp \]
Vapor compression refrigeration cycle
Ex: Reverse Carnot cycle: adiabatic + isothermal processes

Pressure $p$ – Volume $v$ (Ideal gas)

Entropy $S$ – Temperature $T$

$S_2 (< S_1)$

$-Q$

$T_1 (> T_3)$

$+Q$

$T_3$

$p$ (Ideal gas)

$s(p=cte)$
Calculation of isobaric entropy curves: Quasi-direct method

High-pressure calorimetry (DSC-DTA)

\[ S(T, p) = \int \frac{1}{T} \frac{dq(p)}{dT} dT \]

(High-pressure) X-ray diffraction, dilatometry

\[ \Delta S(T, p_{atm} \rightarrow p) = -\int_{p_{atm}}^{p} \left( \frac{\partial V}{\partial T} \right)_p dp \]
Multiferroic systems: Multicaloric effects

Fe$_{49}$Rh$_{51}$: magneto + barocaloric

$(\text{NH}_4)_2\text{SO}_4$: electro + barocaloric


P. Lloveras et al., Nature Comm. 6, 8801 (2015)
Multicaloric effects: Hysteresis reduction

Magnetocaloric effect, with simultaneous application of pressure
- if $dT/dp > 0$, application of pressure on cooling
- if $dT/dp < 0$, application of pressure on heating

Ni-Mn-In-Co

J. Liu et al., Nature Mat. 11, 620 (2012)
Solid-solid first-order phase transitions

Entropy $S$

Temperature $T$

$p_1$

$p = \text{cte}$

Transition at $T_1, p_1$

$S(T)_{p_1}$
Solid-solid first-order phase transitions

Transition at $T_1, p_1$  
Transition at $T_2, p_2$  
Temperature $T$
Solid-solid first-order phase transitions

- Transition at $T_1$, $p_1$
- Transition at $T_2$, $p_2$

Entropy $S$

Temperature $T$

Pressure-induced transition at $T = \text{cte}$

Thermally-induced transition at $p = \text{cte}$

Pressure-induced transition at $T = \text{cte}$

Thermally-induced transition at $p = \text{cte}$
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

![Ordering of spins](image)

| Material        | $|\Delta S_{\text{peak}}| (\text{J K}^{-1} \text{kg}^{-1})$ |
|-----------------|----------------------------------|
| MnNiSi-FeCoGe   | 60                               |
| NiMnIn          | 40                               |
| NiCoMnGaIn      | 20                               |
| GdSiGe          | 20                               |
| LaFeCoSi        | 10                               |
| FeRh            | 5                                |

$p (\text{kbar})$ vs $|\Delta S_{\text{peak}}| (\text{J K}^{-1} \text{kg}^{-1})$
Giant barocaloric materials: transitions with volume changes and large latent heat

- Magnetostructural transitions

- Ferroelectric transitions

\[ \text{Generalized caloric effects:} \]

\[ \begin{align*}
\Delta T & \text{ Adiabatic} \\
\Delta S & \text{ Isothermal}
\end{align*} \]

\[ \int_{Y_1}^{Y_2} \left( \frac{\partial X}{\partial T} \right)_Y dY \]

\[ \Delta S_{\text{isot}} (T, \Delta Y) = \int_{Y_1}^{Y_2} \left( \frac{\partial X}{\partial T} \right)_Y dY \]

\[ \Delta T_{\text{ad}} (T, \Delta Y) = -\int_{Y_1}^{Y_2} \frac{T}{C_Y} \left( \frac{\partial X}{\partial T} \right)_Y dY \]

\[ X : \text{Generalized displacement} \]

\[ TdS = C_Y dT + T \left( \frac{\partial X}{\partial T} \right)_Y dY \]

\[ \sigma : \text{Stress} \rightarrow \text{Elastocaloric} \]

\[ H : \text{Magnetic Field} \rightarrow \text{Magnetocaloric} \]

\[ E : \text{Electric Field} \rightarrow \text{Electrocaloric} \]
**Caloric materials: Ferroic and multiferroic systems**

- **Magnetocaloric**
  - $X$: Magnetization, $M$
  - $Y$: Magnetic Field, $H$
  - High efficiency, quiet
  - First prototypes
  - Large magnetic Fields required: Expensive and difficult to generate
  - Toxic or expensive materials

- **Electrocaloric**
  - $X$: Polarization, $P$
  - $Y$: Electric Field, $E$
  - Thin films: Very large effects
  - Need of fabrication of multilayers
  - Bulk materials: Low breakdown fields

- **Elastocaloric**
  - $X$: Strain, $\varepsilon$
  - $Y$: uniaxial stress, $\sigma$
  - Very large effect
  - Easy to apply
  - Plastic deformation and fatigue: Loss and mechanical breakdown

- **Barocaloric**
  - $X$: Volume $V$
  - $Y$: Pressure $-p$
  - Pressure: easy to generate
  - Powder $\rightarrow$ no fatigue
  - Very Wide range of materials
  - Efficiency? No proof-of-concept yet
Vapor compression refrigeration cycle

Drawback: Leakage of harmful refrigerant fluids

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Leaks
- Long piping (up to hundreds of m in domestic units)
- Large amounts of refrigerant required (up to 50 kg)
- Installation often made by end users
- Mandatory leak inspections are often unfeasible
- Costly waste management
Vapor compression refrigeration cycle

Drawback: Leakage of harmful refrigerant fluids

- In Germany, stationary air conditioning units caused 405 tons of HFC emissions in 2010, or 717400 tons CO₂ equivalent
- 60% of world HFC emissions arise from leaks
- 2050: Almost 10% of global greenhouse gas emissions

Need for a more sustainable technology
Proposal: Solid-state caloric effects