Interplay between phonons and anisotropy drives negative thermal expansion in PbTiO$_3$
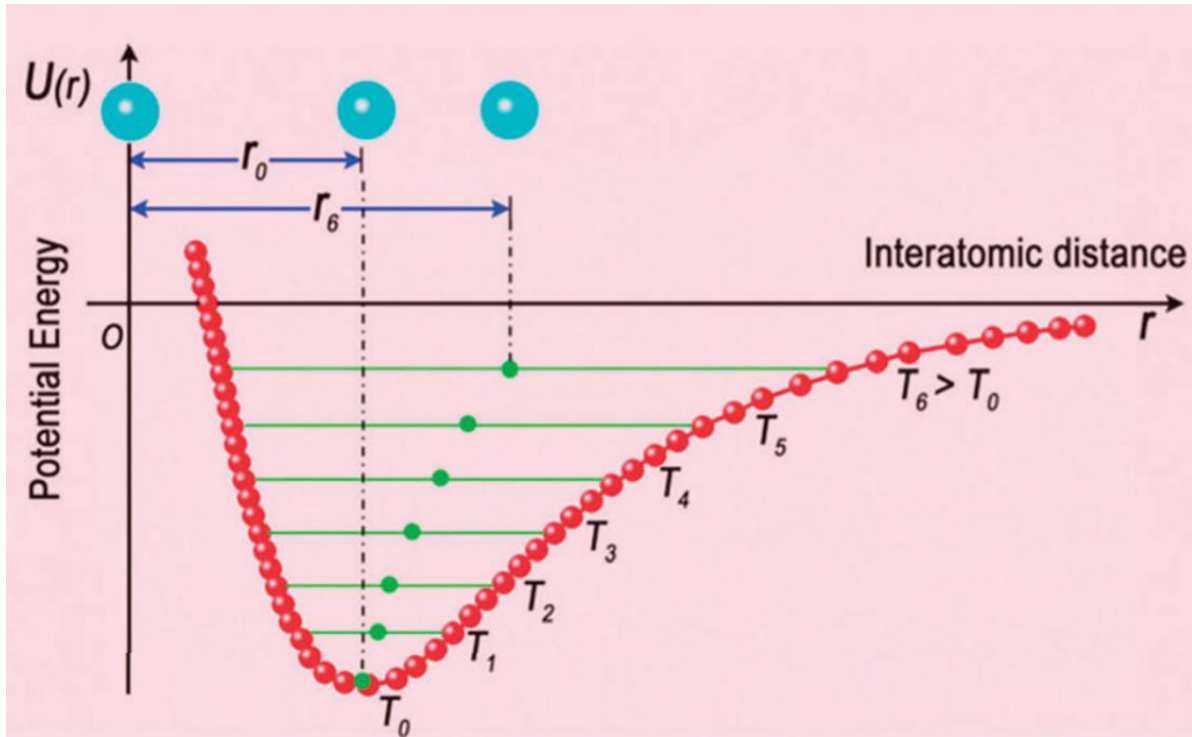
Paper Presentation

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Why do materials expand upon heating?

Fig. Source: Chem. Commun., 2018, 54, 5164

Upon increasing temperature, thermal energy of vibrations increase and thus particles vibrate on a higher potential energy level

Due to the peculiar shape of the interatomic potential curve (which is not harmonic!), the average separation between two atoms increase and therefore we see the material expanding with temperature

$$\alpha_a = \frac{\Delta a}{a \Delta T} \text{ and } \alpha_v = \frac{\Delta V}{V \Delta T}$$

Motivation

- Why do we even need materials with negative α ?

Ans- We need materials whose expansion coefficients can be tailored according to our needs and NTE materials enable this

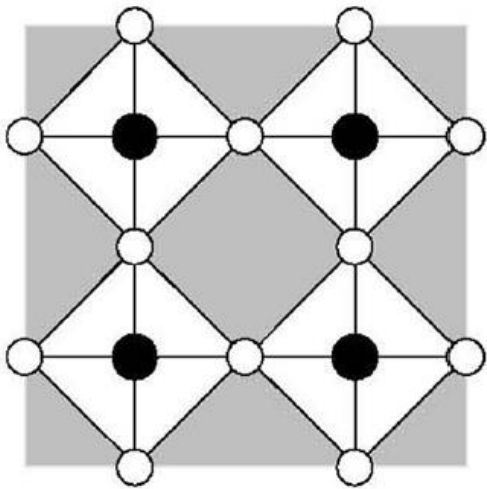Generally, thermal expansion is unwanted, for eg:
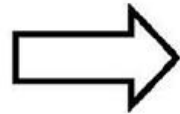
But, in some cases it is necessary!

What causes NTE?

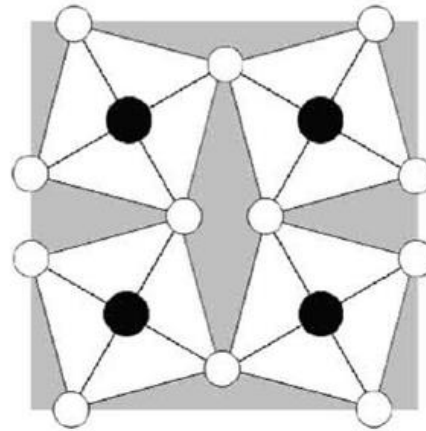## 1. Rigid Unit Phonon Modes

Caused by the rotations of rigid units in the crystals, for eg. The octahedra in perovskites

Volume Contraction

Warming

Can occur in materials with a network like structure like perovskites, zeolites (minerals consisting of hydrated aluminosilicates of Na, K, Ca and Ba), metal-organic frameworks, etc
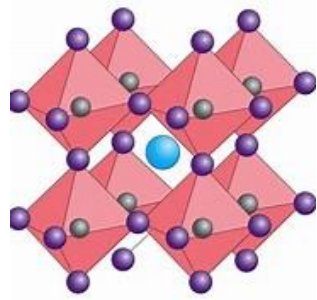
2. Negative Gruneisen Parameters
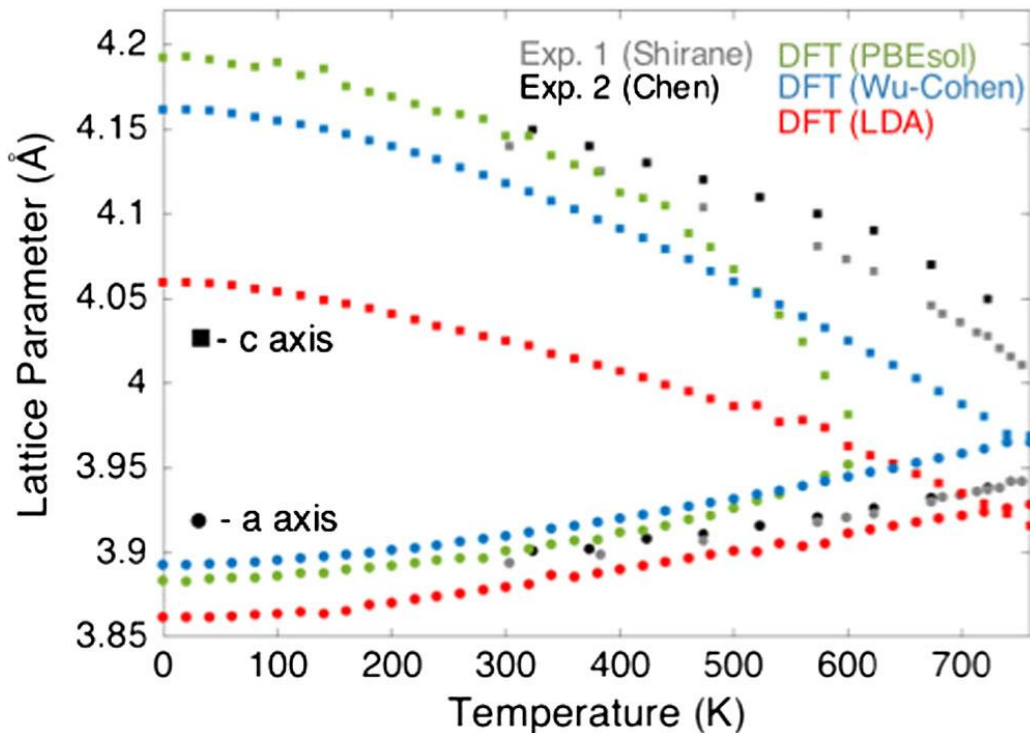
- Gruneisen parameters?

$$\gamma_{\mathbf{k},v} = -\frac{V}{\omega(\mathbf{k},v)}\frac{\partial\omega(\mathbf{k},v)}{\partial V} = -\frac{\partial\left(\ln\omega(\mathbf{k},v)\right)}{\partial(\ln V)}$$

- Upon increasing volume, generally bonds become weaker (cause interatomic distance increase) and thus phonon modes soften
- Under the Quasi Harmonic Approximation, atomic interactions are harmonic but volume dependent
- Thus phonon frequencies can be obtained in a similar way considering lattice constants as a parameter and the gruneisen parameter indicates the dependence of phonon frequencies on volume
- Negative gruneisen parameters indicate hardening of phonon modes with volume

Dove (1993)

PbTiO$_3$

- Cubic at very high temperatures but undergoes phase transition to a tetragonal (P4mm) ferroelectric phase at 760K

- **Tetragonal phase exhibits volumetric NTE** (though only c-axis decreases with temperature while a-axes increase, but overall volume decrease)
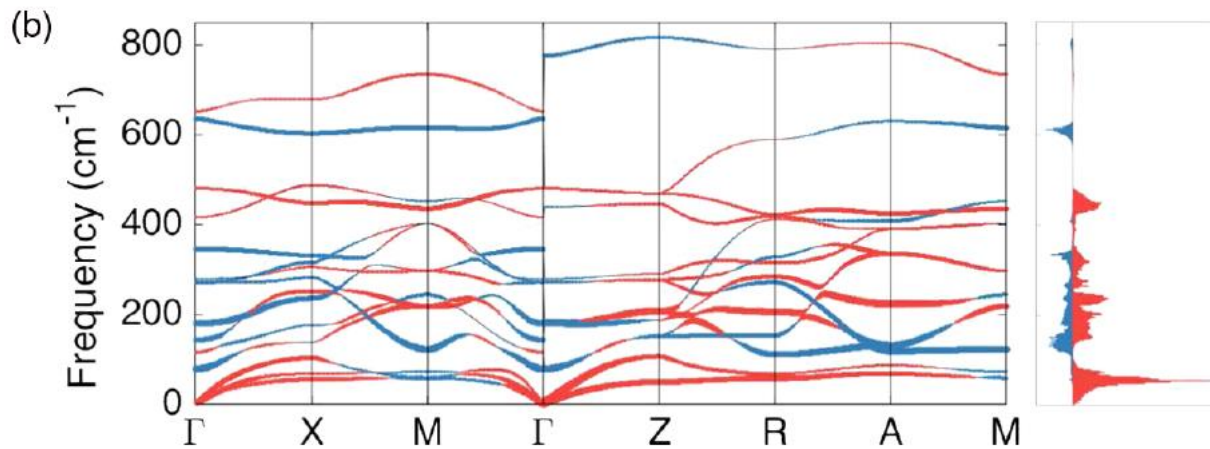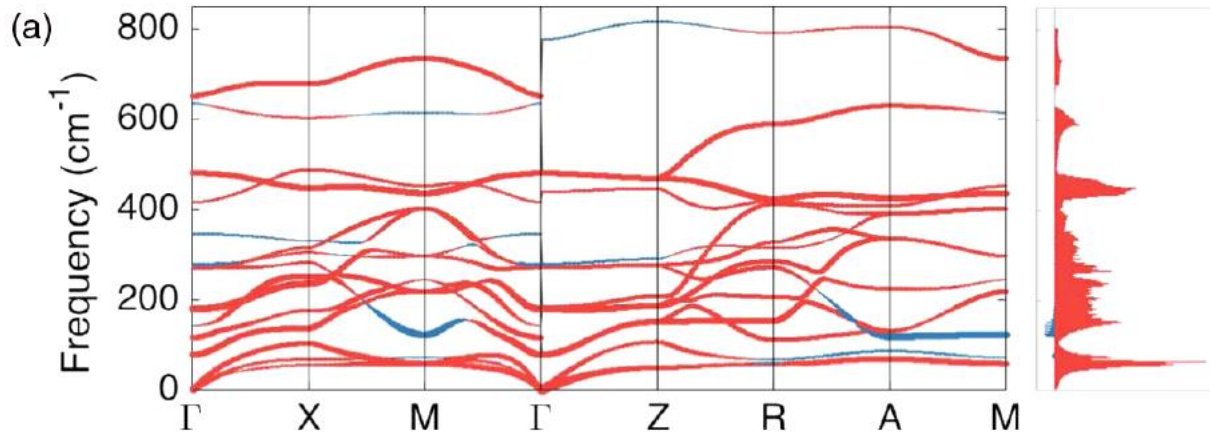

Evolution of lattice parameters as a function of temperature from DFT calculations under the QHA

Obtained value of $\alpha_v = -2.29 \times 10^{-5}\ K^{-1}$

Comparison with experiments: $-1.8 \times 10^{-5}\ K^{-1}$ and $-1.99 \times 10^{-1}\ K^{-1}$

RT Dispersions and Gruneisen Parameters of PbTiO$_3$

(a)

(b)

Since PbTiO3 is not cubic, gruneisen parameters have a tensor form

$$\gamma_{s,\mathbf{k}}^{ij} \equiv -\frac{1}{\omega_{s,\mathbf{k}}}\frac{\partial \omega_{s,\mathbf{k}}}{\partial \varepsilon_{ij}}$$

'bulk' Gruneisen parameter:

$$\gamma_{\text{bulk}}^{ij} = \frac{\sum_{s,\mathbf{k}}\gamma_{s,\mathbf{k}}^{ij}c_{s,\mathbf{k}}}{\sum_{s,\mathbf{k}}c_{s,\mathbf{k}}}$$

$$\gamma_{s,k}^{a} \equiv \gamma_{s,k}^{11}\ ;\ \gamma_{bulk}^{a} = 1.42$$
$$\text{and}$$
$$\gamma_{s,k}^{c} \equiv \gamma_{s,k}^{33}\ ;\ \gamma_{bulk}^{c} = 0.40$$

Phonon dispersions and Pdos where line-thickness is proportional to magnitude of gruneisen parameters and color to the sign. (Red: +ve, Blue: -ve)

(a) - γ^{α} and (b) - γ^{c}

If not –ve GP, then what?

- pDos indicate that low frequency individual phonon modes with +ve GP contribute the most to γ_{bulk}

- Furthermore, the authors find that if these low-frequency modes are kept to be strictly 'harmonic' and the other mode's frequencies are allowed to change with temperature, NTE is suppressed
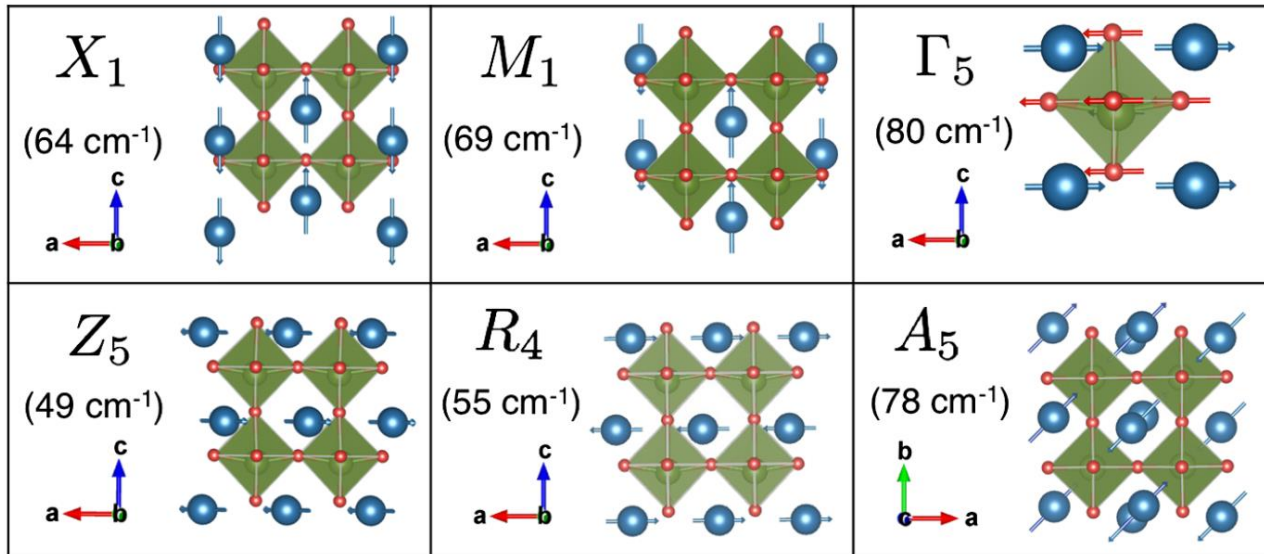
These low frequency modes do not show any RUM like character

α_v for anisotropic materials

For cubic:

$$\alpha_v = \frac{\gamma_{\text{bulk}} C_\eta}{3B} \quad \text{and} \quad \gamma_{s,\mathbf{k}} \equiv -\frac{V}{\omega_{s,\mathbf{k}}} \frac{d\omega_{s,\mathbf{k}}}{dV}$$

For tetragonal:

$$\alpha_a = (C_\eta/V)[(S_{11} + S_{12})\gamma^a_{\text{bulk}} + S_{13}\gamma^c_{\text{bulk}}]$$

$$\alpha_c = (C_\eta/V)[2S_{13}\gamma^a_{\text{bulk}} + S_{33}\gamma^c_{\text{bulk}}]$$

and

$$\alpha_v \equiv 2\alpha_a + \alpha_c$$

$$2(S_{11} + S_{12} + S_{13})\gamma^a_{\text{bulk}} + (S_{33} + 2S_{13})\gamma^c_{\text{bulk}} < 0$$

From this, we can see −ve GP is not required for anisotropic materials since $S_{i,j}$ can be positive or negative

The case with PbTiO$_3$

Author's argument:
It's the tendency of PbTiO3 to expand along a with increasing temperature drives the system to shrink along c which results in volumetric NTE

TABLE I. Selected elements of the compliance tensor for PbTiO$_3$ and SnTiO$_3$ from first-principles calculations in units of 10^{-3} GPa^{-1}.

	S_{11}	S_{12}	S_{13}	S_{33}
PbTiO$_3$	7.44	0.49	−11.94	55.69
SnTiO$_3$	7.79	−1.45	−6.83	31.36

$$\begin{bmatrix} \alpha_a \\ \alpha_a \\ \alpha_c \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{12} & S_{11} & S_{13} \\ S_{13} & S_{13} & S_{33} \end{bmatrix} \begin{bmatrix} \frac{C_\eta \gamma^a_{bulk}}{V} \\ \frac{C_\eta \gamma^a_{bulk}}{V} \\ \frac{C_\eta \gamma^c_{bulk}}{V} \end{bmatrix}$$

Substituting values for α_c:

$$S_{13} = -11.94 \;;\; S_{33} = 55.69 \;;\; \gamma^a_{bulk} = 1.42 \;;\; \gamma^c_{bulk} = 0.40$$

$$\Rightarrow \alpha_c$$

$$= \left(\frac{C_\eta}{V}\right)(2 \times -11.94 \times 1.42 + 55.69 \times 0.40$$

$$= \left(\frac{C_\eta}{V}\right)(-11.6336)$$

Just as a mechanical stress state involving positive stress along both axes could result in negative strain along c due to coupling through S_{13}, thermal stress driven by positive γ^a_{bulk} and γ^c_{bulk} could result in $\alpha_c < 0$, where the sign of α_c depends on a careful balance between all of S_{ij}, γ^a_{bulk}, and γ^c_{bulk}

Anisotropy of compliance tensor was important in the case of tetragonal PbTiO$_3$

Another study on SnTiO$_3$

- To show that compliance tensor is indeed important, the authors computed α_v of SnTiO$_3$

- For SnTiO3: $\gamma_{bulk}^{a} = 3.42$ and $\gamma_{bulk}^{c} = 7.72$. These result in suppressed NTE compared to PbTiO$_3$

Reasons for difference:

- Mass difference cannot be it since the authors did a hypothetical experiment where Pb's mass was replaced with Sn but NTE behaviour was unchanged
- The reason was given that symmetry breaking associated with hybridization of s orbitals (having lone pair) and unfilled p orbitals was more energetically favourable in case of Sn
- This resulted in larger c/a for SnTiO$_3$ (1.18) compared to PbTiO$_3$ (1.08)
- Thus S_{13} is less negative for SnTiO$_3$ compared to PbTiO$_3$ because it is more resistant to further deformation
- To further test this hypothesis, the authors created a hypothetical SnTiO$_3$ structure where c/a was that of PbTiO$_3$. This structure showed NTE!

Conclusions

- RUMs or –ve GPs may not be as important for NTE as previously thought

- Material anisotropy has an important role to play

- For PbTiO$_3$ large –ve S_{13} drives NTE

- The electronic structure which results in a particular c/a is important when considering NTE