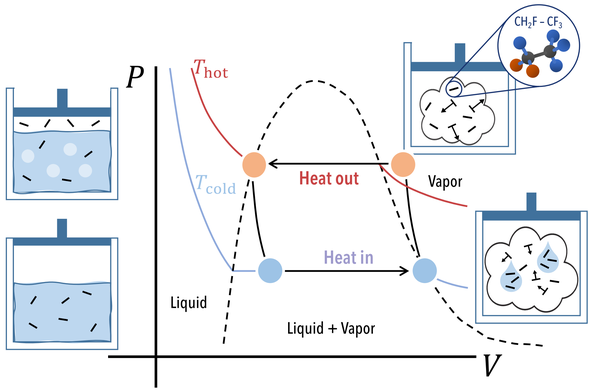
Electric Polarization in High-Entropy Oxides for Electrocaloric Refrigeration

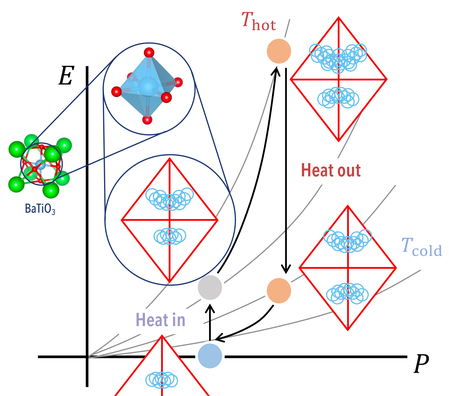
Tara Karimzadeh Sabet, **Ismaila Dabo**
Department of Materials Science and Engineering, The Pennsylvania State University

Motivation

The growing demand for cooling solutions and the need to address global warming have prompted researchers to develop sustainable refrigeration technologies such as electrocaloric devices.



Vapor-Compression Refrigeration

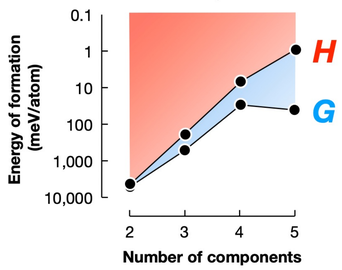


Electrocaloric Refrigeration

- CF_3CH_2F is the most commonly used refrigerant in vapor-compression cooling systems.
- $PbZr_xTi_{1-x}O_3$ is currently among the most efficient materials for electrocaloric cooling.

High-Entropy Oxides

Incorporation of five or more metallic components on the cation sublattice in equal or near-equal proportions leads to a high degree of structural disorder:



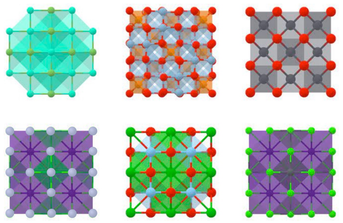
Properties

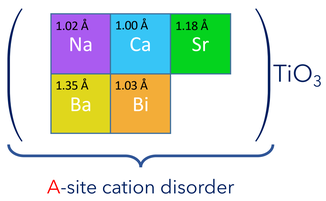
- Tolerance to thermal fluctuations
- High defect tolerance and ion solubility
- High ionic conductivity

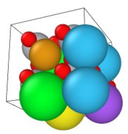
Examples

- $(Na,Bi,Sr,Ba,Ca)TiO_3$
- $Sr(Ti,Nb,Cr,Mo,W)O_3$
- $(Fe,Co,Ni,Cu,Zn)Al_2O_4$
- $(Ce,La,Pr,Sm,Y)O_2$

- High-entropy oxides (HEOs) are obtained by incorporating multiple cations into a single-phase crystal structure, which is stabilized by configurational disorder.
- Ferroelectric HEOs are promising candidates for use as electrocaloric elements due to their tunable properties and high thermal stability.







$(Na,Bi,Sr,Ba,Ca)TiO_3$ is a proposed lead-free alternative to $PbZr_xTi_{1-x}O_3$ for electrocaloric energy conversion.

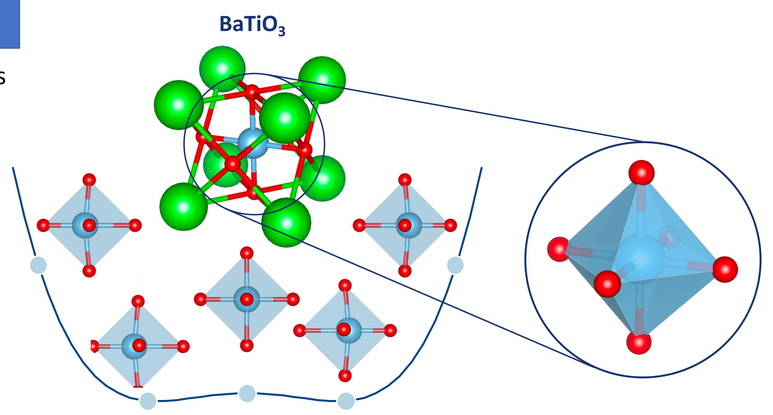
Rost *et al.*, *Nature Communications* **6**, 8485 (2015)
Pu *et al.*, *Applied Physics Letters* **115**, 223901 (2019)
Oses *et al.*, *Nature Review Materials* **5**, 295–309 (2020)

Polarization and Energy Landscapes

- Predicting the ferroelectric response of materials requires a mapping of the potential energy landscape.
- In $BaTiO_3$, the entropic agitation of the titanium atom in the center of the oxygen octahedron increases with temperature.
- The Curie temperature is the critical point where the barrier to polarization switching vanishes.

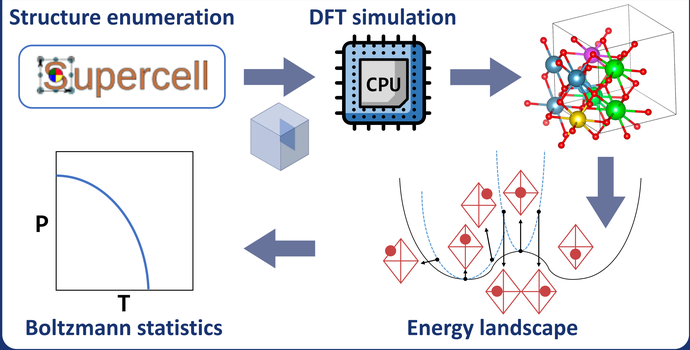
$$U(\boldsymbol{\varepsilon}, T) = \int \mathrm{d}\mathbf{r} E(\mathbf{r}) \mathcal{P}(\mathbf{r}, \boldsymbol{\varepsilon}, T)$$

$$= \frac{\int \mathrm{d}\mathbf{r}^3 E(\mathbf{r}) e^{-(E(\mathbf{r}) - \Omega\boldsymbol{\varepsilon}\cdot P(\mathbf{r}))/k_B T}}{\int \mathrm{d}\mathbf{r}^3 e^{-(E(\mathbf{r}) - \Omega\boldsymbol{\varepsilon}\cdot P(\mathbf{r}))/k_B T}}$$



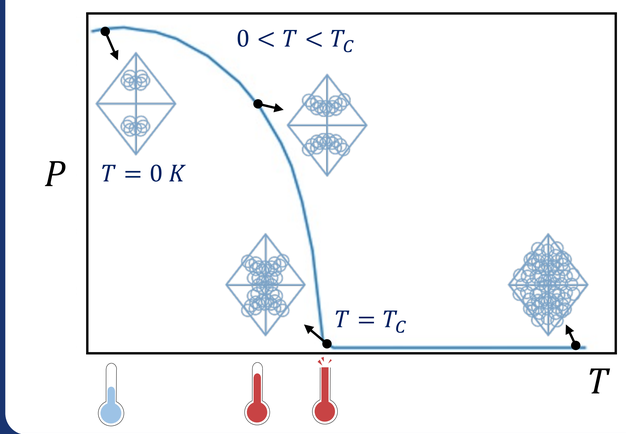
Internal energy as a function of polarization

Methodology



Temperature-Dependent Ferroelectricity

We predicted the temperature-dependent polarization of $BaTiO_3$ and are investigating the role of configurational entropy on dP/dT, which controls electrocaloric efficiency.

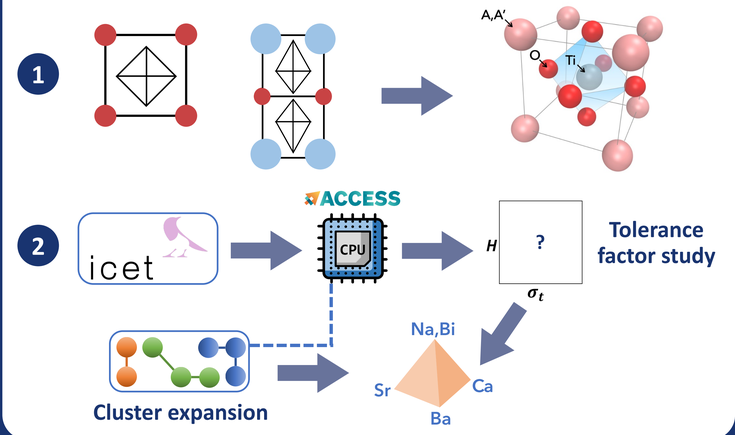


Conclusion and Future Work

Key takeaways:

- In HEOs, the presence of multiple cations introduces disorder that alters local crystal structure and polarization behavior.
- Calculating energy landscapes allows us to predict the temperature-dependent ferroelectric polarization.
- We anticipate that **$(Na,Bi,Sr,Ba,Ca)TiO_3$** will exhibit moderate dependence of polarization as a function of temperature, resulting in higher cooling efficiency.

Plan for future studies:



Acknowledgments

Center for Nanoscale Science, supported by the NSF (DMR-2011839).

Penn State ICS-ACI Supercomputing Systems