Temperature-Dependent Compositional Stability and Electric Polarization of High-Entropy Oxides in Electrocaloric Cooling Applications

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High-Entropy Oxides

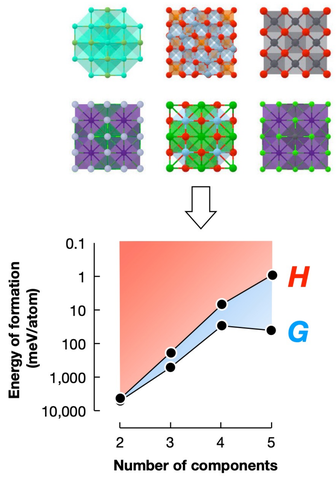
By integrating theory and experiments, we aim to design and develop materials for efficient solid-state refrigeration technologies. Incorporation of five or more metal components on the cation sublattice in high-entropy oxides (HEOs) allows access to an entirely new space for materials discovery in novel elemental combinations and phases.

Properties

- Stability (tolerance to thermal fluctuations)
- Heat capacity (degeneracy of energy landscape)
- Defect tolerance and ion solubility (diversity of coordination and oxidations)
- Ion conductivity (tolerance to local distortions)

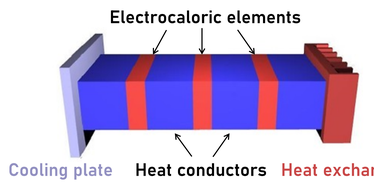
Applications

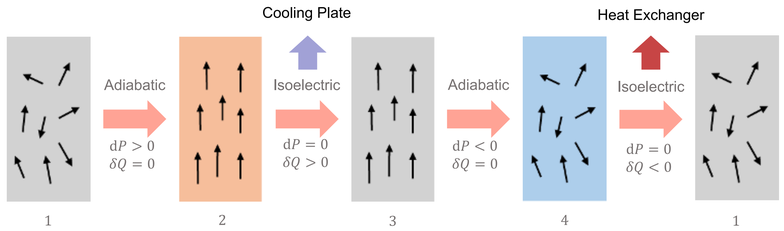
- Transparent conductors, e.g., $Sr(TiNbCrMoW)_{1/4}O_3$
- **Electrocalorics, e.g., $(CaSrBaNaBi)_{1/5}TiO_3$**
- Fast-ion conductors, e.g., $(CeLaPrSmY)_{1/5}O_2$
- Multifunctional catalysts, e.g., $(FeCoNiCuZn)Al_2O_4$



Electrocaloric Effect

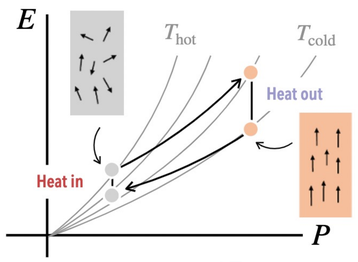
The electrocaloric (EC) effect is currently being explored as a promising method for environmentally-friendly solid-state refrigeration techniques.





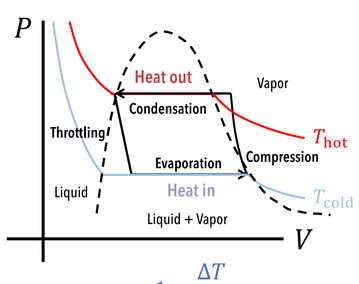
A strong change in temperature with a small change in polarization and, thus, a larger surface area, increases the electrocaloric (EC) performance of the material.

Electrocaloric Refrigeration



$$\eta = 1 - \frac{\Delta T}{\langle T \rangle}$$

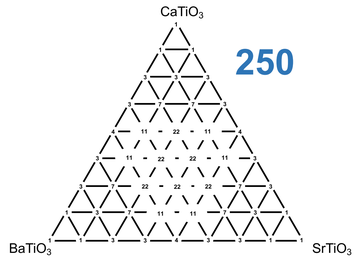
Vapor-Compression Refrigeration



$$\eta = 1 - \frac{\Delta T}{\langle T \rangle}$$

Compositional Stability

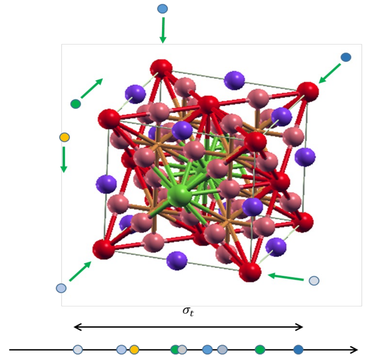
Investigating the compositional stability of HEOs via density-functional theory calculations facilitates the study of complex, multicomponent electrocaloric materials. However, there are many configurations that must be considered.



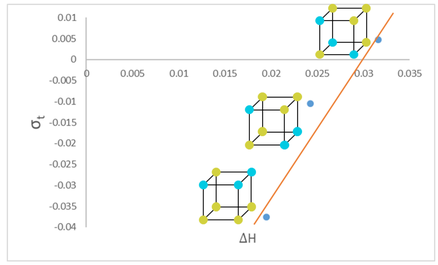
Case studies on the material system of interest suggest an increase in the enthalpy of mixing with an increase in the spread σ_t of the tolerance factor.

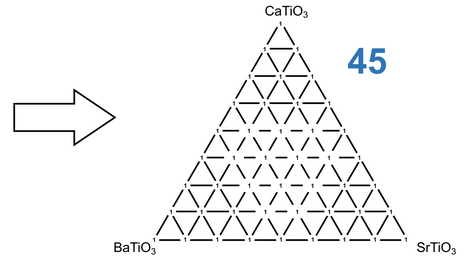
A *directional* Goldschmidt's tolerance factor t is introduced as a geometric parameter correlating with the enthalpy of mixing. The spread of the geometric tolerance factor is indicative of stability.

$$t = \left\langle \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \right\rangle$$



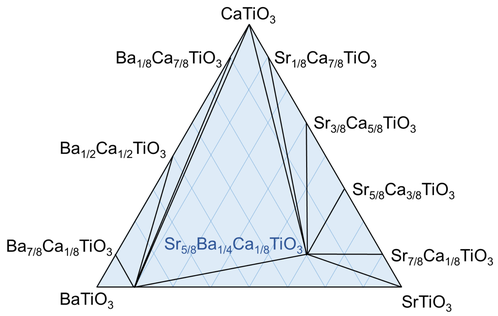
Validating this correlation will greatly reduce the complexity of calculations through identifying the structures with the lowest energy, which will be the main target of the Convex-Hull diagram used in compositional stability analysis.

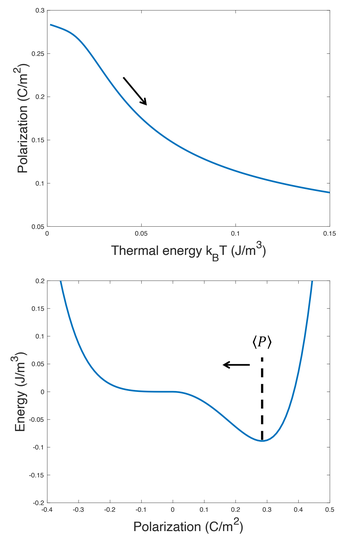




Polarization in EC Cooling

The temperature-dependent polarization can be determined based on the energy calculated from density-functional theory for the stable compositions and the lowest-energy configurations for each of them.





Future Work

- Investigating the effect of high-entropy stabilization on the B-cation sublattice
- Calculating the configurational and vibrational entropy contributions to the free energy
- Assessing newly-developed (machine-learning-based) tolerance factors
- Elucidating the nature of domain walls in high-entropy perovskites

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