First-Principles Studies of Perovskite Compounds for Thermoelectric Applications

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Introduction

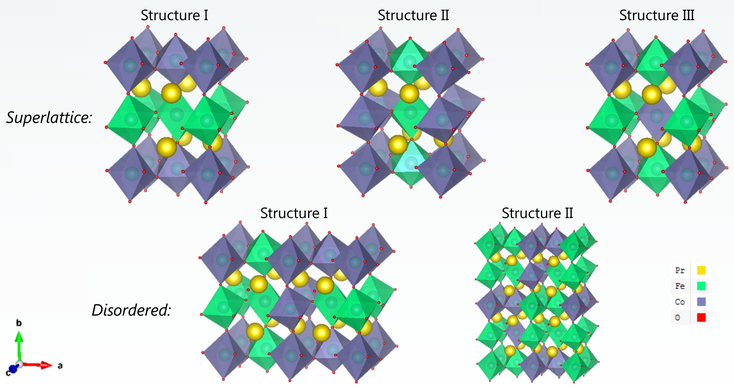
Computational modeling techniques have been used to provide detailed insights into the structure-property relationships of materials. We have collaborated with the National Institute of Standards and Technology (NIST) to develop various perovskite compounds with desired thermoelectric properties. We have used density functional theory-based approaches to study structural stability and electrical properties of $R_2(FeCo)O_6$ perovskite compounds (R = Pr, Nd, Sm, Eu and Gd), for which Fe and Co randomly occupy the B-site. Superlattice and locally disordered phases have been compared through a total energy minimization approach.

Objectives

- Compare stability of superlattice and disordered phases
- Calculate electronic density of states for the stable phases
- Determine methodology for estimating electrical conductivity properties

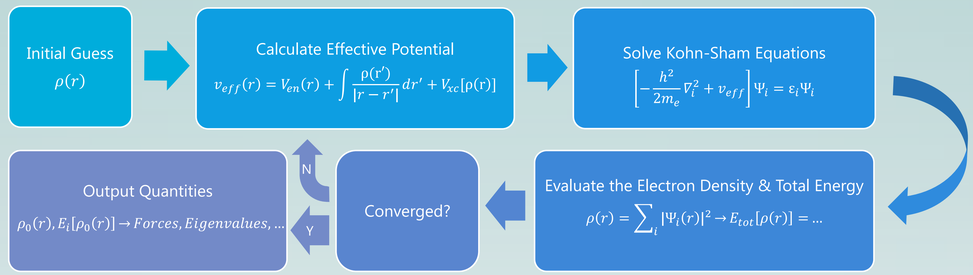
Perovskite Compounds

- Perovskite: any material with the same type of crystal structure as calcium titanate ($CaTiO_3$)
- Expand perovskite unit cell: the center atom alternates between two different atoms [1]



Methods

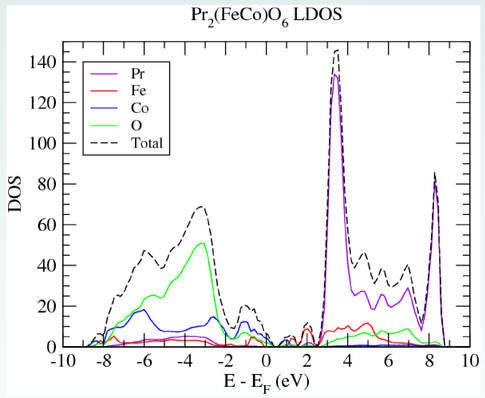
Vienna ab-initio simulation package (VASP) has been performed to optimize geometry and structure. Due to the ferromagnetic natures of Fe and Co, we have supplied initial magnetic moments of $4\mu_B$ and $1\mu_B$, respectively. Additional input parameters include a conjugate electronic minimization algorithm and a 400 eV cutoff energy for plane-wave basis set. In order to study electronic properties, DFT+U has been used to account for d and f orbitals of certain elements.



Results

Below are theoretical lattice parameters, cell volumes, and bond lengths for $Pr_2(FeCo)O_6$ options as well as experimental values from a TEM. The local density of states (LDOS) is shown for stable disordered structure II.

$Pr_2(FeCo)O_6$ Lattice Parameters				
	a (Å)	*b (Å)*	*c (Å)*	*Volume (Å³)*
Experimental	5.466	7.702	5.443	229.17
Superlattice				
Structure I	5.528	7.567	5.282	220.96
Structure II	5.642	7.499	5.209	220.36
Structure III	5.533	7.563	5.301	221.81
Disordered				
Structure I	5.493	7.487	5.462	224.64
Structure II	5.614	7.495	5.463	229.87



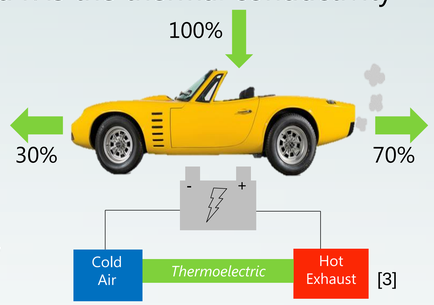
$Pr_2(FeCo)O_6$ Bond Lengths (Å)								
	Pr-O4	*Pr-O4*	*Pr-O5*	*Pr-O5*	*Pr-O5*	*Co/Fe-O4*	*Co/Fe-O5*	*Co/Fe-05*
Experimental	2.370	2.484	2.540	2.790	2.369	1.970	1.986	1.978
Superlattice								
Structure III	2.284	2.350	2.414	2.634	2.414	2.000	2.037	2.033
Disordered								
Structure I	2.282	2.282	2.406	2.671	2.406	1.963	2.027	1.999
Structure II	2.293	2.275	2.418	2.647	2.422	1.976	2.084	2.051

Discussion and Conclusions

- Increasing disorder yields lattice parameters and bond lengths similar to experimental values.
- Total energy minimization calculations indicate that disordered phase of $Pr_2(FeCo)O_6$ is more stable than its superlattice, agreeing well with experimental observation.
- Overlapping peaks in the DOS plot suggest bonding covalency in the $R_2(FeCo)O_6$ structure.
- Our electronic structure calculations suggest that $Pr_2(FeCo)O_6$ is semiconducting with an electronic band gap of 0.43 eV.

Material Application: Thermoelectrics

- Thermoelectric (TE) effect: direct conversion of temperature differences to electric voltage
- TE figure of merit: $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature and κ is the thermal conductivity
- TE material uses: power generation and refrigeration
- Factors affecting TE advancement: cost, thermal stability, and toxicity [2]



References

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[2] Sugahara, Tohru, Michitaka Ohtaki, and Katsuaki Suganuma. "La Doped Effects on Structure and Thermoelectric Properties of Sr2MnMoO6 Double-perovskite Oxides."*Journal of Asian Ceramic Societies* 1.3 (2013): *ScienceDirect*.

[3] The Nanoemeter Structure Consortium at Lund University, http://www.nano.lth.se/research/nano-energy/thermoelectrics?layoutmode=print

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