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Final Report: Discovering and Understanding Striking Phenomena in Dipolar Materials

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5b. GRANT NUMBER

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Fayetteville, AR 72701 -1201

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13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Laurent Bellaiche
UU	UU	UU	UU		19b. TELEPHONE NUMBER 479-575-6425

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as of 24-Apr-2020

Agency Code:

Proposal Number: 68166MS **Agreement Number: W911NF-16-1-0227**
INVESTIGATOR(S):

Name: Ph.D. Laurent Bellaiche
Email: laurent@uark.edu
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Principal: Y

Organization: **University of Arkansas**
Address: 210 Administration Building, Fayetteville, AR 727011201
Country: USA
DUNS Number: 191429745 EIN: 716003252
Report Date: 30-Jun-2020 Date Received: 23-Apr-2020
Final Report for Period Beginning 01-May-2016 and Ending 31-Mar-2020
Title: Discovering and Understanding Striking Phenomena in Dipolar Materials
Begin Performance Period: 01-May-2016 **End Performance Period:** 31-Mar-2020
Report Term: 0-Other
Submitted By: Ph.D. Laurent Bellaiche Email: laurent@uark.edu
Phone: (479) 575-6425
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 3 **STEM Participants:** 3

Major Goals: The main objective of this proposal is to discover and understand striking phenomena in dipolar materials.

Accomplishments: Please see pdf document in the Upload section

Training Opportunities: To reach our goals, we developed and used first-principles-based schemes, as well as collaborated with International scientists.

Results Dissemination: Via publications and talks given at International conferences.

Honors and Awards: For an undergraduate student:

- Honors College Travel Grant from the University of Arkansas awarded to Davis Campbell (Fall 2019).

- Davis Campbell, Honors Studies in Physics, Fall 2019, ``Finite Temperature Magnetic Properties of Rare-Earth Iron Garnets."

- Best Poster presented by a student at the 2020 Workshop on Fundamental Physics of Ferroelectrics and Related Materials; Silver Spring, MD, January 26-January 29, 2020; ``Finite Temperature Magnetic Properties of Rare Earth-Iron Garnets,'' Davis Campbell

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Laurent Bellaiche
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:

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National Academy Member: N
Other Collaborators:

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.118.147601
Volume: 118 Issue: 14 First Page #: 147601
Date Submitted: 4/19/17 12:00AM Date Published: 4/5/17 5:00AM
Publication Location: New York, New York, USA
Article Title: Fluctuations and Topological Defects in Proper Ferroelectric Crystals
Authors: Sergei Prokhorenko, Yousra Nahas, Laurent Bellaiche
Keywords: Topological defects
Abstract: Homotopy theory and first-principles-based effective Hamiltonian simulations are combined to investigate the stability of topological defects in proper ferroelectric crystals. We show that, despite a nearly trivial topology of the order parameter space, these materials can exhibit stable topological point defects in their tetragonal polar phase and stable topological line defects in their orthorhombic polar phase. The stability of such defects originates from a novel mechanism of topological protection related to finite-temperature fluctuations of local dipoles.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: PHYSICAL REVIEW B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.94.214113
Volume: 94 Issue: 7 First Page #: 214113
Date Submitted: 4/19/17 12:00AM Date Published: 12/27/16 12:00PM
Publication Location: New York, New York, USA
Article Title: Towards multicaloric effect with ferroelectrics
Authors: Yang Liu, Guangzu Zhang, Qi Li, Laurent Bellaiche, James F. Scott, Brahim Dkhil, and Qing Wang
Keywords: multicaloric
Abstract: Here, we report the multi caloric effect in BaTiO3 single crystals driven simultaneously by mechanical and electric fields and described via a thermodynamic phenomenological model. It is found that the multicaloric behavior is mainly dominated by the mechanical field rather than the electric field, since the paraelectric-to-ferroelectric transition is more sensitive to mechanical field than to electric field. The use of uniaxial stress competes favorably with pressure due to its much higher caloric strength and negligible elastic thermal change. It is revealed that multicaloric response can be significantly larger than just the sum of mechanocaloric and electrocaloric effects in temperature regions far above the Curie temperature but cannot exceed this limit near the Curie temperature. Our results also show the advantage of the multicaloric effect over the mechanically mediated electrocaloric effect or electrically mediated mechanocaloric effect.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Scientific Report
Publication Identifier Type: DOI Publication Identifier: 10.1038/srep37529
Volume: 6 Issue: 1 First Page #: 37529
Date Submitted: 4/19/17 12:00AM Date Published: 11/25/16 6:00AM
Publication Location: London, UK
Article Title: Tuning the Weak Ferromagnetic States in Dysprosium Orthoferrite
Authors: Shixun Cao, Lei Chen, Weiyao Zhao, Kai Xu, Guohua Wang, Yali Yang, Baojuan Kang, Hongjian Zhao,
Keywords: phase diagrams
Abstract: Here, we report an extensive investigation of a high-quality DyFeO3 single crystal in which the induced Dy3+ magnetization (FDy) has a natural tendency to be antiparallel to Fe3+ sublattice magnetization (FFe) within a large temperature window. Moreover, we find that specific variations of temperature and applied magnetic fields allow us to make FDy parallel to FFe, or force a spin-flip transition in FFe, among other effects. We found three different magnetic states that respond to temperature and magnetic fields, i.e. linear versus constant or, alternatively, presenting either behavior depending on the history of the sample. An original magnetic field-versustemperature phase diagram is constructed to indicate the region of stability of the different magnetic phases, and to reveal the precise conditions yielding sudden spin switching and reversals. Knowledge of such a phase diagram is of potential importance to applications in spintronics and and magnetic devices.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: PHYSICAL REVIEW B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.94.180102
Volume: 94 Issue: 1 First Page #: 180102
Date Submitted: 4/19/17 12:00AM Date Published: 11/3/16 5:00AM
Publication Location: New York, New York, USA
Article Title: Effects of atomic short-range order on properties of the PbMg1/3Nb2/3O3 relaxor ferroelectric
Authors: Sergey Prosandeev and L. Bellaiche
Keywords: relaxors
Abstract: The effect of atomic short-range order on the macroscopic and microscopic properties of the prototype of relaxor ferroelectrics, that is, lead magnesium niobate Pb(Mg1/3Nb2/3)O3 (PMN), is studied via the combination of an annealing technique and a large-scale effective Hamiltonian method. The investigated short-range order gradually varies from the case of fully disordered solid solutions to the situation for which the first three nearest-neighboring shells of the B lattice of PMN adopt a rocksalt ordering between a sublattice made of pure Nb ions and a randomly distributed sublattice consisting of 23 of Mg and 13 of Nb. The characteristic temperaturesof relaxor ferroelectrics (namely, the Burns, so-called T?, and depolarizing temperatures) significantly increasewhen strengthening this short-range chemical order, which is accompanied by an overall enhancement of the size of the polar nanoregions as well as of some antiferroelectric interactions.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: J. Phys.: Condens. Matter
Publication Identifier Type: DOI Publication Identifier: 10.1088/0953-8984/28/47/475901
Volume: 28 Issue: 1 First Page #: 475901
Date Submitted: 4/19/17 12:00AM Date Published: 9/23/16 5:00AM
Publication Location: London, UK
Article Title: Special quasirandom structures for perovskite solid solutions
Authors: Zhijun Jiang, Yousra Nahas, Bin Xu, Sergey Prosandeev, Dawei Wang and Laurent Bellaiche
Keywords: disordered alloys
Abstract: Special quasirandom structures (SQS) are presently generated for disordered (A?1?xA▼x)BX3 and A(B?1?xB▼x)X3 perovskite solid solutions, with x = 1/2 as well as 1/3 and 2/3. These SQS configurations are obtained by imposing that the so-called Cowley parameters are as close to zero as possible for the three nearest neighboring shells. They are used here within effective Hamiltonian schemes to predict various properties, which are then compared to those associated with large random supercells, in a variety of compounds, namely (Ba1?xSrx)TiO3, Pb(Zr1?xTix)O3, Pb(Sc0.5Nb0.5)O3, Ba(Zr1?xTix)O3, Pb(Mg1/3Nb2/3)O3 and (Bi1?xNdx)FeO3. It is found that these SQS configurations can reproduce many properties of large random supercells of most of these disordered perovskite alloys, below some finite material-dependent temperature.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Communications
Publication Identifier Type: DOI Publication Identifier: 10.1038/ncomms15944
Volume: 8 Issue: 1 First Page #: 15944
Date Submitted: 7/6/17 12:00AM Date Published: 6/20/17 5:00AM
Publication Location: England
Article Title: Microscopic origins of the large piezoelectricity of leadfree (Ba,Ca)(Zr,Ti)O3
Authors: Yousra Nahas, Alireza Akbarzadeh, Sergei Prokhorenko, Sergey Prosandeev, Raymond Walter, Igor Kc
Keywords: lead-free piezoelectrics
Abstract: In light of directives around the world to eliminate toxic materials in various technologies, finding lead-free materials with high piezoelectric responses constitutes an important current scientific goal. As such, the recent discovery of a large electromechanical conversion near room temperature in (1┐x)Ba(Zr0.2Ti0.8)O3┐x(Ba0.7Ca0.3)TiO3 compounds has directed attention to understanding its origin. Here, we report the development of a large-scale atomistic scheme providing a microscopic insight into this technologically promising material. We find that its high piezoelectricity originates from the existence of large fluctuations of polarization in the orthorhombic state arising from the combination of a flat free-energy landscape, a fragmented local structure, and the narrow temperature window around room temperature at which this orthorhombic phase is the equilibrium state. In addition to deepening the current knowledge on piezoelectricity, these findings have the potential to guide
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: J. Phys.: Condens. Matter
Publication Identifier Type: DOI Publication Identifier: 10.1088/1361-648X/aa6eff
Volume: 29 Issue: 1 First Page #: 254001
Date Submitted: 7/6/17 12:00AM Date Published: 5/18/17 5:00AM
Publication Location: England
Article Title: Toy model for uncommon spin–orbit-driven spin-torque terms
Authors: Charles Paillard, Raymond Walter, Surendra Singh, Brahim Dkhil and L Bellaiche
Keywords: angular magneto electric coupling, spin–orbit, spin torques
Abstract: A toy model combining the angular magneto electric (AME) coupling Hamitonian (Mondal et al 2015 Phys. Rev. B 92 100402) with long-range magnetic dipolar interactions is used to investigate spin-torque phenomena in a magnetic spin valve. It is found that such model (1) gives rise to spin-torque expressions that are analogous in form to those of the common spin-transfer torques; but also (2) predicts additional spin-torque terms, which are generated by an electrical current oriented along unconventional, in-plane directions. The magnitude of the AME induced terms is estimated and the conditions under which they may contribute significantly are explored.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.96.014114
Volume: 96 Issue: 1 First Page #: 014114
Date Submitted: 8/8/17 12:00AM Date Published: 7/24/17 8:50PM
Publication Location: New York
Article Title: Electrocaloric effects in the lead-free Ba(Zr,Ti)O3 relaxor ferroelectric from atomistic simulations
Authors: Zhijun Jiang, Sergei Prokhorenko, Sergey Prosandeev, Y. Nahas, D. Wang, Jorge Iniguez, E. Defay, L.
Keywords: electrocaloric effects
Abstract: Atomistic effective Hamiltonian simulations were used to investigate electrocaloric (EC) effects in the lead-free Ba(Zr0.5Ti0.5)O3 (BZT) relaxor ferroelectric. We found that the EC coefficient varies nonmonotonically with the field at any temperature, presenting a maximum that can be traced back to the behavior of BZT's polar nanoregions. We also introduced a simple Landau-based model that reproduces the EC behavior of BZT as a function of field and temperature, and which is directly applicable to other compounds. Finally, we confirmed that, for low temperatures (i.e., in nonergodic conditions), the usual indirect approach to measure the EC response provides an estimate that differs quantitatively from a direct evaluation of the field-induced temperature change.
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Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: PHYSICAL REVIEW LETTERS
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.119.117601
Volume: 119 Issue: 1 First Page #: 117601
Date Submitted: 9/21/17 12:00AM Date Published: 9/12/17 5:00AM
Publication Location: New York
Article Title: Emergent Berezinskii-Kosterlitz-Thouless Phase in Low-Dimensional Ferroelectrics
Authors: Y. Nahas, S. Prokhorenko, I. Kornev, L. Bellaiche
Keywords: topological defects, BKT transition, ferroelectrics
Abstract: Using first-principles-based simulations merging an effective Hamiltonian scheme with scaling, symmetry, and topological arguments, we find that an overlooked Berezinskii-Kosterlitz-Thouless (BKT) phase sustained by quasicontinuous symmetry emerges between the ferroelectric phase and the paraelectric one of BaTiO3 ultrathin film, being under tensile strain. Not only do these results provide an extension of BKT physics to the field of ferroelectrics, but they also unveil their nontrivial critical behavior in low dimensions.
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Journal: Advanced Materials
Publication Identifier Type: DOI Publication Identifier: 10.1002/adma.201702375
Volume: 29 Issue: 1 First Page #: 1702375
Date Submitted: 8/2/18 12:00AM Date Published: 10/24/17 11:39AM
Publication Location: New York
Article Title: Nanoscale Bubble Domains and Topological Transitions in Ultrathin Ferroelectric Films
Authors: Qi Zhang, Lin Xie, Guangqing Liu, Sergei Prokhorenko, Yousra Nahas, Xiaoqing Pan, Laurent Bellaiche
Keywords: bubbles
Abstract: Observation of a new type of nanoscale ferroelectric domains, termed as “bubble domains”—laterally confined spheroids of sub-10 nm size with local dipoles self-aligned in a direction opposite to the macroscopic polarization of a surrounding ferroelectric matrix—is reported. The bubble domains appear in ultrathin epitaxial PbZr0.2Ti0.8O3/SrTiO3/PbZr0.2Ti0.8O3 ferroelectric sandwich structures due to the interplay between charge and lattice degrees of freedom. The existence of the bubble domains is revealed by high-resolution piezoresponse force microscopy (PFM), and is corroborated by aberration-corrected atomic-resolution scanning transmission electron microscopy mapping of the polarization displacements. An incommensurate phase and symmetry breaking is found within these domains resulting in local polarization rotation and hence impart a mixed Néel–Bloch-like character to the bubble domain walls.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.97.024113
Volume: 97 Issue: 1 First Page #: 024113
Date Submitted: 8/2/18 12:00AM Date Published: 1/26/18 12:43PM
Publication Location: New York
Article Title: Energetics of oxygen-octahedra rotations in perovskite oxides from first principles
Authors: Peng Chen, Mathieu N. Grisolia, Hong Jian Zhao, Otto E. Gonzalez-Vazquez, L. Bellaiche, Manuel Bibe
Keywords: tiltings
Abstract: We used first-principles methods to investigate the energetics of oxygen-octahedra rotations in ABO3 perovskite oxides. Our work provides a comprehensive discussion and reference data on these all-important and abundant materials, which will be useful to better understand existing compounds as well as to identify new strategies for materials engineering.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.97.104110
Volume: 97 Issue: 1 First Page #: 104110
Date Submitted: 8/2/18 12:00AM Date Published: 3/30/18 11:47AM
Publication Location: New York
Article Title: Giant response in the prototypical Pb(Mg,Nb)O3 relaxor ferroelectric from atomistic simulations
Authors: Zhijun Jiang, Y. Nahas, S.Prokhorenko, S. Prosandeev, D. Wang, Jorge Iniguez, L. Bellaiche
Keywords: electrocaloric effects
Abstract: An atomistic effective Hamiltonian was used to investigate electrocaloric (EC) effects of Pb (Mg1/3Nb2/3)O3 relaxor ferroelectrics in its ergodic regime, and subject to electric fields applied along the pseudocubic [111] direction.
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Volume: 120 Issue: 1 First Page #: 177601
Date Submitted: 8/2/18 12:00AM Date Published: 4/23/18 11:52AM
Publication Location: New York
Article Title: Topological defects with distinct dipole configurations in PbTiO3/SrTiO3 multilayer films
Authors: Lu Lu, Yousra Nahas, Ming Liu, Hongchu Du, Zhijun Jiang, Shengping Ren, Dawei Wang, Lei Jin, Serge
Keywords: topological defects
Abstract: In collaboration with the experimental group of Dr Jia (Juelich, Germany), distinct and novel features of nanometric electric topological defects, including dipole waves and dipole disclinations, were revealed in the PbTiO3 layers of PbTiO3/SrTiO3 multilayer films by means of quantitative high-resolution scanning transmission electron microscopy. These original dipole configurations were confirmed and explained by atomistic simulations and have the potential to act as functional elements in future electronics.
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Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.121.027601
Volume: 121 Issue: 1 First Page #: 027601
Date Submitted: 8/2/18 12:00AM Date Published: 7/9/18 11:56AM
Publication Location: New York
Article Title: Intrinsic Origin of Enhancement of Ferroelectricity in SnTe Ultrathin Films
Authors: Kai Liu, Jinlian Lu, Silvia Picozzi, Laurent Bellaiche, Hongjun Xiang
Keywords: thin films; Curie temperature
Abstract: Previous studies showed that, as ferroelectric films become thinner, their Curie temperature (Tc) and polarization below Tc both typically decrease. In contrast, a recent experiment [Chang et al., Science 353, 274 (2016)] observed that atomic-thick SnTe films have a higher Tc than their bulk counterpart, which was attributed to extrinsic effects. We found, using first-principles calculations, that the 0K energy barrier for the polarization switching (which is a quantity directly related to Tc) is higher in most investigated defect-free SnTe ultrathin films than that in bulk SnTe, and that the 5-unit-cell (UC) SnTe thin film has the largest energy barrier as a result of an interplay between hybridization interactions and Pauli repulsions. Further simulations, employing a presently developed effective Hamiltonian, confirm that freestanding, defect-free SnTe thin films have a higher Tc than bulk SnTe, except for the 1-UC case. Our work, therefore, demonstrates the possibility to intrinsic
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: npj Computational Materials
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1038/s41524-018-0141-4
Volume: 5 Issue: 1 First Page #: 6
Date Submitted: 1/15/19 12:00AM Date Published: 1/8/19 10:00PM
Publication Location: England
Article Title: Strain engineering of electro-optic constants in ferroelectric materials
Authors: Charles Paillard, Sergei Prokhorenko, Laurent Bellaiche
Keywords: electrooptic
Abstract: Electro-optic effects allow control of the ow of light using electric fields, and are of utmost importance for today's information andcommunication technologies, such as TV displays and fiber optics. The search for large electro-optic constants in films is essential to the miniaturization and increased efficiency of electro-optic devices. In this work, we demonstrate that strain-engineering in PbTiO3 films allows to selectively choose which electro-optic constant to improve. Unclamped electro-optic constants larger than 100 pmV?1 are predicted, either by driving the softening of an optical phonon mode at a phase transition boundary under tensile strain, or by generating the equivalent of a negative pressure via compressive strain to obtain extremely large piezoelectric constants. In particular, a r33 electro-optic coefficient twice as large as the one of the commonly used LiNbO3 electro-optic material is found here when growing PbTiO3 on the technologicallyimportant Si substrate.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: npj Computational Materials
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1038/s41524-018-0134-3
Volume: 4 Issue: 1 First Page #: 75
Date Submitted: 1/15/19 12:00AM Date Published: 12/12/18 10:05PM
Publication Location: England
Article Title: Tailoring properties of hybrid perovskites by domain-width engineering with charged walls
Authors: Lan Chen, Charles Paillard, Hong Jian Zhao, Jorge Íñiguez, Yurong Yang and Laurent Bellaiche
Keywords: hybrid perovskites
Abstract: Charged ferroelectric domain walls are fascinating electrical topological defects that can exhibit unusual properties. Here, in thesearch for novel phenomena, we perform and analyze first-principles calculations to investigate the effect of domain width onproperties of domains with charged walls in the photovoltaic material consisting of methylammonium lead iodide hybridperovskite. We report that such domains are stable and have rather low domain wall energy for any investigated width (that is, up to 13 lattice constants). Increasing the domain width first linearly decreases the electronic band gap from ?1.4 eV to about zero (which therefore provides an efficient band-gap engineering), before the system undergoes an insulator-to-metal transition and then remains metallic (with both the tail-to-tail and head-to-head domain walls being conductive) for the largest widths. All these results can be understood in a simple way.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: npj Computational Materials
Publication Identifier Type: DOI Publication Identifier: doi:10.1038/s41524-018-0115-6
Volume: 4 Issue: 1 First Page #: 57
Date Submitted: 1/15/19 12:00AM Date Published: 11/5/18 10:10PM
Publication Location: England
Article Title: Interplay between Kitaev interaction and single ion anisotropy in ferromagnetic CrI3 and CrGeTe3 monolayers
Authors: Changsong Xu, Junsheng Feng, Hongjun Xiang and Laurent Bellaiche
Keywords: 2D metallic layers
Abstract: Magnetic anisotropy is crucially important for the stabilization of two-dimensional (2D) magnetism, which is rare in nature buthighly desirable in spintronics and for advancing fundamental knowledge. Recent works on CrI3 and CrGeTe3 monolayers not onlyled to observations of the long-time-sought 2D ferromagnetism, but also revealed distinct magnetic anisotropy in the two systems, namely Ising behavior for CrI3 versus Heisenberg behavior for CrGeTe3. Such magnetic difference strongly contrasts with structuraland electronic similarities of these two materials, and understanding it at a microscopic scale should be of large benefits. Here, firstprinciples calculations are performed and analyzed to develop a simple Hamiltonian, to investigate magnetic anisotropy of CrI3 and CrGeTe3 monolayers. The anisotropic exchange coupling in both systems is surprisingly determined to be of Kitaev-type.
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Journal: PHYSICAL REVIEW B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.98.104101
Volume: 98 Issue: 1 First Page #: 104101
Date Submitted: 1/15/19 12:00AM Date Published: 9/5/18 2:14AM
Publication Location:
Article Title: Quantum-fluctuation-stabilized orthorhombic ferroelectric ground state in lead-free piezoelectric (Ba, Ca)(Zr, Ti)O3
Authors: Alireza Akbarzadeh, Kumar Brajesh, Yousra Nahas, Naveen Kumar, Sergei Prokhorenko, Diptikanta Sw
Keywords: quantum effects
Abstract: We numerically investigate the phase diagram of the giant-piezoelectric (1 ? x)Ba(Zr0.2Ti0.8) O3-x (Ba0.7Ca0.3)TiO3 system, treating the ions either as classical objects (via classical Monte Carlo or CMCsimulations) or quantum mechanically (via path-integral quantum Monte Carlo or PI-QMC simulations).It is found that PI-QMC not only provides a better agreement with available experimental data for thetemperature-composition phase diagram, but also leads to the existence of an orthorhombic ground state ina narrow range of composition, unlike CMC that “only” yields ground states of rhombohedral or tetragonal symmetry. X-ray powder diffraction experiments are further conducted at 20 K. They confirm the occurrence of a quantum-fluctuation-induced orthorhombic state for some compositions and therefore validate the PI-QMC prediction.
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Volume: 2 Issue: 1 First Page #: 084404
Date Submitted: 1/15/19 12:00AM Date Published:
Publication Location:
Article Title: Structural and magnetic transitions accompanied by large responses in epitaxial Sr0.5Ba0.5MnO3 films
Authors: Temuujin Bayaraa, Yurong Yang, Hong Jian Zhao, Jorge Íñiguez, and L. Bellaiche
Keywords: magnetoelectrics
Abstract: The effect of epitaxial compressive and tensile strains on the physical properties of multiferroic Sr0. 5Ba0.5MnO3films is investigated via the use of ab initio calculations. Striking phenomena are predicted. Examples include(1) the existence of a previously overlooked strain-induced low-symmetry phase bridging the tetragonal(compressively strained) and orthorhombic (tensile-strained) ferroelectric structures, which exhibits a very largepiezoelectric response; (2) a first-order magnetic transitionwithin the tetragonal polar state, which is accompanied by remarkable changes in polarization and out-of-plane lattice constant; (3) the existence of a state that is both ferromagnetic and ferroelectric with a large polarization and axial ratio at large enough compressive strain; and (4) the possibility to induce a structural phase transition between states of different symmetries (e.g., between tetragonal and monoclinic, or between orthorhombic and monoclinic) by applying a magnetic field.

Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Emerging Photovoltaic Materials, (105–140) 2019 Scrivener Publishing LLC
Publication Identifier Type: Other Publication Identifier: None
Volume: 1 Issue: 1 First Page #: 105
Date Submitted: 7/9/19 12:00AM Date Published: 1/9/19 9:10PM
Publication Location: New York
Article Title: Photovoltaics in Ferroelectric Materials: Origin, Challenges and Opportunities
Authors: Charles Paillard, Gregory Geneste, Laurent Bellaiche, Jens Kreisel, Marin Alexe, Brahim Dkhil
Keywords: photovoltaic; ferroelectrics
Abstract: Ferroelectric materials are polar, which requires inversion symmetry to be absent. As a result, they exhibit exotic photovoltaic properties caused by the so-called Bulk Photovoltaic effect occurring in non-centrosymmetric materials. Unlike common photovoltaic effects present in, for instance, p–n junction-based solar cells, the Bulk Photovoltaic effect relies on non-thermalized photoexcited carriers and can, as a result, break the so-called Shockley-Queisser thermodynamic limit. Various factors, such as metal-ferroelectric interface, defects, or bandgap contribute, alter or enhance the capacity of ferroelectric materials to convert visible light into electrical energy. In addition, the wealth of properties of ferroelectric (and multiferroic materials) may allow to achieve functionalities beyond the simple conversion into electricity. A review of all these effects is done here.

Acknowledged Federal Support: **Y**

RPPR Final Report
as of 24-Apr-2020

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.99.104103
Volume: 99 Issue: 1 First Page #: 104103
Date Submitted: 7/9/19 12:00AM Date Published: 3/5/19 12:00PM
Publication Location: New York
Article Title: Magnetoelastic and magnetoelectric couplings across the antiferromagnetic transition in multiferroic BiFeO3
Authors: Mariusz Lejman, Charles Paillard, Vincent Juve, Gwenaelle Vaudel, Nicolas Guiblin, Laurent Bellaiche, I
Keywords: couplings; multiferroics
Abstract: Clear anomalies in the lattice thermal expansion (deviation from linear variation) and elastic properties (softening of the sound velocity) at the antiferromagnetic-to-paramagnetic transition are observed in the prototypical multiferroic BiFeO3 using a combination of picosecond acoustic pump-probe and high-temperature x-ray diffraction experiments. Similar anomalies are also evidenced using second-principles calculations supporting our experimental findings. Those calculations, in addition to a simple Landau-like model we also developed, allow us to understand the elastic softening and lattice change at TN as a result of magnetostriction combined with electrostrictive and magnetoelectric couplings, which renormalize the elastic constants of the high-temperature reference phase when the critical TN temperature is reached.

Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.122.097601
Volume: 122 Issue: 1 First Page #: 097601
Date Submitted: 7/9/19 12:00AM Date Published: 3/7/19 6:00AM
Publication Location: New York
Article Title: Novel dynamical magnetoelectric effects in multiferroics
Authors: S. Omid Sayedaghaee, Bin Xu, Sergey Prosandeev, Charles Paillard and L. Bellaiche
Keywords: Dynamics; new quasi-particles
Abstract: An atomistic effective Hamiltonian scheme is employed within molecular dynamics simulations to investigate how the electrical polarization and magnetization of the multiferroic BiFeO3 respond to time-dependent ac magnetic fields of various frequencies, as well as to reveal the frequency dependency of the dynamical (quadratic) magnetoelectric coefficient. The quadratic magnetoelectric coupling constant is monotonic and almost dispersionless in the sub-THz range when strain is fixed. In contrast, when the homogeneous strain can fully relax, two additional low-frequency and strain-mediated oscillations emerge in the time-dependent behavior of the polarization and magnetization, which result in resonances in the quadratic magnetoelectric coefficient. Such additional oscillations consist of a mixing between acoustic phonons, optical phonons, and magnons, and reflect the existence of a new quasiparticle that can be coined an “electroacoustic magnon.”

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RPPR Final Report
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Ferroelectrics
Publication Identifier Type: DOI Publication Identifier: 10.1080/00150193.2018.1474650
Volume: 535 Issue: 1 First Page #: 93
Date Submitted: 7/9/19 12:00AM Date Published: 3/11/19 5:00AM
Publication Location: New York
Article Title: Temperature and electric field control of the bandgap in electrotoroidic nanocomposites by large-Scale ab initio methods
Authors: R. Walter, S. Prokhorenko, Z. Gui, Y. Nahas, L.-W. Wang, and L. Bellaiche
Keywords: Topological defects
Abstract: An effective Hamiltonian scheme combined with a GPU implementation of the linear-scaling three-dimensional fragment (LS3DF) method is used to compute electronic properties of two topological objects in a nanocomposite: an electrical vortex coexisting with spontaneous electrical polarization over a wide temperature range and an electrical skyrmion over a range of applied electric fields. Temperature control of the vortex provides substantially larger range of control of bandgap and band alignment than field control of the skyrmion. Using temperature and electric fields to manipulate polarization and bond angle distortion in different component materials provides a handle for bandgap engineering in such nanostructures.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Advanced Functional Materials
Publication Identifier Type: DOI Publication Identifier: 10.1002/adfm.201808573
Volume: 1 Issue: 1 First Page #: 1808573
Date Submitted: 7/9/19 12:00AM Date Published: 4/1/19 8:00PM
Publication Location: New York
Article Title: Deterministic switching of ferroelectric bubble nanodomains
Authors: Qi Zhang, Sergei Prokhorenko, Yousra Nahas, Laurent Bellaiche, Alexei Gruverman, Nagarajan Valano
Keywords: topological defects
Abstract: Here, the deterministic and reversible transformation of nanoscale ferroelectric bubbles into cylindrical domains using a scanning probe microscopy (SPM) approach is demonstrated. The bubble domains —sub-10 nm spheroid topological structures with rotational polarization— can be erased by applying a mechanical force via the SPM tip. Application of an electrical pulse with a specific combination of amplitude and duration can recreate the bubble domain state. This combination of mechanical and electrical passes is essential for realization of reversible transformation as application of only electrical pulses results in complete erasure of the bubble domain state. Effective Hamiltonian-based simulations reproduce phase sequences for both the mechanical and electric passes and confirm the intrinsic nature of these transitions. This simple and effective pathway for switching between various topological defect states may be exploited for emergent devices.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.122.227601
Volume: 122 Issue: 1 First Page #: 227601
Date Submitted: 7/9/19 12:00AM Date Published: 6/4/19 3:00PM
Publication Location: New York
Article Title: Ferroelectricity with Asymmetric Hysteresis in Metallic LiOsO3 Ultrathin Films
Authors: Jinlian Lu, Gong Chen, Wei Luo, Jorge Iniguez, Laurent Bellaiche, Hongjun Xiang
Keywords: metals; ferroelectrics
Abstract: Bulk LiOsO3 was experimentally identified as a “ferroelectric” metal where polar distortions coexist with metallicity [Shi et al., Nat. Mater. 12, 1024 (2013)]. It is generally believed that polar displacements in a ferroelectric metal cannot be switched by an external electric field. Here, via comprehensive density functional theory calculations, we demonstrated that a two-unit cell-thick LiOsO3 thin film exhibits a ferroelectric ground state having an out-of-plane electric dipole moment that can be switched by an external electric field. Moreover, its dipole moment-versus-electric field hysteresis loop is asymmetric because only surface Li ions’ displacements are reversed by the external electric field whereas the field-induced force on inner Li atoms is nearly fully screened by itinerant electrons. As a relevant by-product of our study, we also extended the concept of “Born effective charge” to finite metallic systems, and show its usefulness to rationalize the observed effects.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physics: Condensed Matter
Publication Identifier Type: DOI Publication Identifier: 10.1088/1361-648X/aaa51f
Volume: 30 Issue: 1 First Page #: 073001
Date Submitted: 7/9/19 12:00AM Date Published: 1/22/19 6:00AM
Publication Location: New York
Article Title: Photostriction and elasto-optic response in multiferroics and ferroelectrics from first principles
Authors: Yurong Yang, Charles Paillard, Bin Xu, and L. Bellaiche
Keywords: light-matter interactions
Abstract: This work reviews a series of recent first-principles studies devoted to the description of the interaction of light and strain in ferroelectric and multiferroic materials. Specifically, the modelling schemes used in these works to describe the so-called photostriction and elasto-optic effects are presented, in addition to the results and analysis provided by these ab-initio calculations. In particular, the large importance of the piezoelectric effect in the polar direction in the photostriction of ferroelectric materials is stressed. Similarly, the occurrence of low-symmetry phases in lead titanate thin films under tensile strain is demonstrated to result in large elasto-optic constants. In addition, first-principle calculations allow to gain microscopic knowledge of subtle effects, for instance in the case of photostriction, where the deformation potential effect in directions perpendicular to the polar axis is shown to be almost as significant as the piezoelectric effect.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Applied Physics Reviews
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.5046559
Volume: 5 Issue: 1 First Page #: 041108
Date Submitted: 7/9/19 12:00AM Date Published: 12/6/18 12:00PM
Publication Location: New York
Article Title: Epitaxial ferroelectric oxide thin films for optical applications
Authors: D. Sando, Yurong Yang, Charles Paillard, B. Dkhil, L. Bellaiche, V. Nagarajan
Keywords: optics; oxides
Abstract: Ferroelectrics are non-centrosymmetric crystalline materials that possess a spontaneous polarization that can be switched by an electric field. The electric-field-dependent optical response of these materials makes them important for optical devices, such as modulators or beam deflectors. In the inexorable drive to miniaturization, the concept of integrated thin film optical devices has led to the incorporation of ferroelectric thin films on single-crystal substrates. These structures have appealing electro-optic modulation characteristics, interesting strain-dependent band-gaps and refractive index, as well as promising possibilities for solar harvesting. Here, we review the work on epitaxial ferroelectric (FE) films for optical applications. We show that FE thin film materials are attractive for integrated electro-optic modulators and then show that epitaxial strain can be used to enhance the FE and optical functionality of films.

Acknowledged Federal Support: **Y**

Contract Information

Contract Number	W911NF-16-1-0027
Title of Research	Discovering and Understanding Striking Phenomena in Dipolar Materials
Principal Investigator	Laurent Bellaiche
Organization	University of Arkansas

Let me first sincerely thank ARO and Dr. Pani (Chakrapani) Varanasi for this award that allows my group to conduct many studies we were interested in. It has been a real pleasure to work under this ARO sponsorship, and I hope that we will continue (to have the honors) to be sponsored by ARO.

Secondly, this final report is organized as follows: Section I provides the list of all publications during the award period; Section II details the recent studies conducted since the last annual report; and Section III lists the award and honors received during the award period

I. List of all publications

- 1) "Inverse transition of labyrinthine domain patterns in ferroelectric thin films," Y. Nahas, S. Prokhorenko, J. Fischer, B. Xu, C. Carrétéro, S. Prosandeev, M. Bibes, S. Fusil, B. Dkhil, V. Garcia and L. Bellaiche, Nature 577, 47 (2020).
2) "Macroscopic and Microscopic Structures of Cesium Lead Iodide Perovskite from Atomistic Simulations," Lan Chen, Bin Xu, Yurong Yang and L. Bellaiche, Advanced Functional Materials 1909496 (2020).
- 3) "Universality and origin of ultrashort intrinsic negative dielectric permittivity," Sergey Prosandeev, Charles Paillard, B. Xu and L. Bellaiche, Physical Review B 101, 024111 (2020).

- 4) "Temperature dependence of polar modes in hybrid improper ferroelectrics," Kinnary Patel, Sergey Prosandeev, Bin Xu and L. Bellaiche, Physical Review B 100, 214107 (2019).
- 5) "Rashba-like spin-orbit and strain effects in tetragonal PbTiO3," R. Arras, J. Gosteau, H. J. Zhao, C. Paillard, Y. Yang, and L. Bellaiche, Physical Review B 100, 174415 (2019).
- 6) "Designing multifunctionality via assembling dissimilar materials: Epitaxial AlN/ScN superlattices," Zhijun Jiang, Charles Paillard, David Vanderbilt, Hongjun Xiang and L. Bellaiche, Physical Review Letters 123, 096801 (2019).
- 7) "Photoinduced phase transitions in ferroelectrics," Charles Paillard, Engin Torun, Ludger Wirtz, Jorge Íñiguez and Laurent Bellaiche, Physical Review Letters 123, 087601 (2019).
- 8) "Ferroelectricity with Asymmetric Hysteresis in Metallic LiOsO3 Ultrathin Films," Jinlian Lu, Gong Chen, Wei Luo, Jorge Íñiguez, Laurent Bellaiche, Hongjun Xiang, Physical Review Letters 122, 227601 (2019).
- 9) "Deterministic switching of ferroelectric bubble nanodomains," Qi Zhang, Sergei Prokhorenko, Yousra Nahas, Laurent Bellaiche, Alexei Gruverman and Nagarajan Valanoor, Advanced Functional Materials 1808573 (2019)
- 10) "Magnetoelastic and magnetoelectric couplings across the antiferromagnetic transition in multiferroic BiFeO3,"Mariusz Lejman, Charles Paillard, Vincent Juvé, Gwenaelle Vaudel,

Nicolas Guiblin, Laurent Bellaiche, Michel Viret, Vitalyi E. Gusev, Brahim Dkhil and Pascal Ruello, Physical Review B 99, 104103 (2019).
11) "Novel dynamical magnetoelectric effects in multiferroics," S. Omid Sayedaghaee, Bin Xu, Sergey Prosandeev, Charles Paillard and L. Bellaiche, Physical Review Letters 122, 097601 (2019).
- 12) "Strain engineering of electro-optic constants in ferroelectric materials," Charles Paillard, Sergei Prokhorenko and L. Bellaiche, npj computational Materials 5, 6 (2019).
- 13) "Photovoltaics in Ferroelectric Materials: Origin, Challenges and Opportunities," Charles Paillard, Grégory Geneste, Laurent Bellaiche, Jens Kreisel, Marin Alexe and Brahim Dkhil, Advanced Materials Book Series; Santosh Kurinec (ed.), Emerging Photovoltaic Materials, (105-140) 2019 Scrivener Publishing
- 14) "Epitaxial ferroelectric oxide thin films for optical applications," D Sando, Y Yang, C Paillard, B Dkhil, L Bellaiche, V Nagarajan, Applied Physics Reviews 5 (4), 041108 (2018).
- 15) "Temperature and electric field control of the bandgap in electrotoroidic nanocomposites by large-Scale ab initio methods," R. Walter, S. Prokhorenko, Z. Gui, Y. Nahas, L.-W. Wang, and L. Bellaiche, Ferroelectrics 535, 93 (2018).
- 16) "Tailoring properties of hybrid perovskites by domain-width engineering with charged walls,"Lan Chen, Charles Paillard, Hong jian Zhao, Jorge Íñiguez, Yurong Yang, and L. Bellaiche, npj Computational Materials 4, 75 (2018).
- 17) "Interplay between Kitaev interaction and single ion anisotropy in ferromagnetic CrI3 and CrGeTe3 monolayers," Changsong Xu, Junsheng Feng, Hongjun Xiang and L. Bellaiche, npj Computational Materials 4, 57 (2018).
- 18) "Quantum-fluctuation-stabilized orthorhombic ferroelectric ground state in lead-free piezoelectric (Ba,Ca)(Zr,Ti)O3," Alireza Akbarzadeh, Kumar Brajesh, Yousra Nahas, Naveen Kumar, Sergei Prokhorenko, Diptikanta Swain, Sergey Prosandeev, Raymond Walter, Igor Kornev, Jorge Íñiguez, Brahim Dkhil, Rajeev Ranjan and L. Bellaiche, Physical Review B 98, 104101 (2018).
- 19) "Structural and magnetic transitions accompanied by large responses in epitaxial Sr0.5Ba0.5MnO3 films," T. Bayaraa, Yurong Yang, Hong Jian Zhao, Jorge Íñiguez, L. Bellaiche, Physical Review Materials 2, 084404 (2018).
- 20) "Intrinsic Origin of Enhancement of Ferroelectricity in SnTe Ultrathin Films," Kai Liu, Jinlian Lu, Silvia Picozzi, Laurent Bellaiche, and Hongjun Xiang, Physical Review Letters 121, 027601 (2018).
- 21) "Topological defects with distinct dipole configurations in PbTiO3/SrTiO3 multilayer films," Lu Lu, Yousra Nahas, Ming Liu, Hongchu Du, Zhijun Jiang, Shengping Ren, Dawei Wang, Lei Jin, Sergei Prokhorenko, Chun-Lin Jia and Laurent Bellaiche, Physical Review Letters 120, 177601 (2018).
- 22) "Giant electrocaloric response in the prototypical Pb(Mg,Nb)O3 relaxor ferroelectric from atomistic simulations," Zhijun Jiang, Y. Nahas, S.Prokhorenko, S. Prosandeev, D. Wang, Jorge Íñiguez, and L. Bellaiche, Physical Review B 97, 104110 (2018).
- 23) "Energetics of oxygen-octahedra rotations in perovskite oxides from first principles," Peng Chen, Mathieu N. Grisolia, Hong Jian Zhao, Otto E. Gonzalez-Vazquez, L. Bellaiche, Manuel Bibes, Bang-Gui Liu, and Jorge Íñniguez, Physical Review B 97, 024113 (2018); Editors Suggestion.

- 24) “Nanoscale Bubble Domains and Topological Transitions in Ultrathin Ferroelectric Films,” Qi Zhang, Lin Xie, Guangqing Liu, Sergei Prokhorenko, Yousra Nahas, Xiaoqing Pan, Laurent Bellaiche, Alexei Gruverman and Nagarajan Valanoor, Advanced Materials 29,1702375 (2017)
- 25) “Emergent Berezinskii-Kosterlitz-Thouless phase in low-dimensional ferroelectrics,” Y. Nahas, S. Prokhorenko, I. Kornev, and L. Bellaiche, Physical Review Letters 119, 117601 (2017).
- 26) “Electrocaloric effects in the lead-free Ba(Zr,Ti)O3 relaxor ferroelectric from atomistic simulations,” Zhijun Jiang, Sergei Prokhorenko, Sergey Prosandeev, Y. Nahas, D. Wang, Jorge Íñiguez, E. Defay and L. Bellaiche, Physical Review B 96, 014114 (2017).
- 27) “Microscopic origins of the large piezoelectricity of leadfree (Ba,Ca)(Zr,Ti)O3,” Yousra Nahas, Alireza Akbarzadeh, Sergei Prokhorenko, Sergey Prosandeev, Raymond Walter, Igor Kornev, Jorge Íñiguez and L. Bellaiche, Nature Communications 8, 15944 (2017).
-28) “Toy Model for uncommon spin-orbit-driven spin-torque terms,” Charles Paillard, Raymond Walter, Surendra Singh, Brahim Dkhil and L. Bellaiche, Journal of Physics: Condensed Matter 29, 254001 (2017).
-29) “Fluctuations and topological defects in proper ferroelectric crystals,” S. Prokhorenko, Y. Nahas and L. Bellaiche, Physical Review Letters 118, 147601 (2017).

II. Studies since the last annual report

The following progresses towards our goals have been made from August 01, 2019 to March 30, 2020:

- “Inverse transition of labyrinthine domain patterns in ferroelectric thin films,” Y. Nahas, S. Prokhorenko, J. Fischer, B. Xu, C. Carrétéro, S. Prosandeev, M. Bibes, S. Fusil, B. Dkhil, V. Garcia and L. Bellaiche, Nature 577, 47 (2020).

Phase separation is a cooperative process, the kinetics of which underpin the orderly morphogenesis of domain patterns on mesoscopic scales. Systems of highly degenerate frozen states may exhibit the rare and counterintuitive inverse-symmetry breaking phenomenon. Proposed a century ago4, inverse transitions have been found experimentally in disparate materials, ranging from polymeric and colloidal compounds to high-transition-temperature superconductors, proteins, ultrathin magnetic films, liquid crystals and metallic alloys, with the notable exception of ferroelectric oxides, despite extensive theoretical and experimental work on the latter. Here we show that following a subcritical quench, the non-equilibrium self-assembly of ferroelectric domains in ultrathin films of Pb(Zr0.4Ti0.6)O3 results in a maze, or labyrinthine pattern, featuring meandering stripe domains. Furthermore, upon increasing the temperature, this highly degenerate labyrinthine phase undergoes an inverse transition whereby it transforms into the less-symmetric parallel-stripe domain structure, before the onset of paraelectricity at higher temperatures. We find that this phase sequence can be ascribed to an enhanced entropic contribution of domain walls, and that domain straightening and coarsening is predominantly driven by the relaxation and diffusion of topological defects. Computational modelling and experimental observation of the inverse dipolar transition in BiFeO3 suggest the universality of the phenomenon in ferroelectric oxides. The multitude of self-patterned states and the various topological defects that they embody may be used beyond current domain and domain-wall-based technologies by enabling fundamentally new design principles and topologically enhanced

functionalities within ferroelectric films.

DOI: 10.1038/s41586-019-1845-4; published: January 01, 2020

- “Macroscopic and Microscopic Structures of Cesium Lead Iodide Perovskite from Atomistic Simulations,” Lan Chen, Bin Xu, Yurong Yang and L. Bellaiche, Advanced Functional Materials 1909496 (2020).

A first-principles-based effective Hamiltonian is developed and employed to investigate finite-temperature structural properties of a prototype of perovskite halides, that is CsPbI3. Such simulations, when using first-principles-extracted coefficients, successfully reproduce the existence of an orthorhombic Pnma state and its iodine octahedral tilting angles around room temperature. However, they also yield a direct transformation from Pnma to cubic Pm3m upon heating, unlike measurements that reported the occurrence of an intermediate long-range-tilted tetragonal P4/mbm phase in-between the orthorhombic and cubic phases. Such disagreement, which may cast some doubts about the extent to which first-principle methods can be trusted to mimic hybrid perovskites, can be resolved by “only” changing one short-range tilting parameter in the whole set of effective Hamiltonian coefficients. In such a case, some reasonable values of this specific parameter result in the predictions that i) the intermediate P4/mbm state originates from fluctuations over many different tilted states; and ii) the cubic Pm3m phase is highly locally distorted and develops strong transverse antiphase correlation between first-nearest neighbor iodine octahedral tiltings, before undergoing a phasetransition to P4/mbm under cooling.

DOI: 10.1002/adfm.201909496; published: March 10, 2020

- ``Universality and origin of ultrashort intrinsic negative dielectric permittivity," Sergey Prosandeev, Charles Paillard, B. Xu and L. Bellaiche, Physical Review B 101, 024111 (2020).
DOI: 10.1103/PhysRevB.101.024111; published 24 January 2020

By recasting the definition of the dielectric constants in terms of currents, as well as using atomistic simulations and analytical derivations, we showed that the dielectric permittivity can be negative at an ultrashort timescale, under perfect screening conditions and for very different materials and switching mechanisms, in-line with recent experiments and modelings. In particular, we found that this effect can be due to a previously overlooked phenomenon of postswitching polarization oscillations.We also derived practical analytical formulas that can be experimentally checked.

- ``Temperature dependence of polar modes in hybrid improper ferroelectrics," Kinnary Patel, Sergey Prosandeev, Bin Xu and L. Bellaiche, Physical Review B 100, 214107 (2019).
DOI: 10.1103/PhysRevB.100.214107; published 6 December 2019

An atomistic effective Hamiltonian, along with a presently developed analytical model, are employed to investigate and analyze low-frequency polar, antipolar and antiferrodistortive phonons at finite temperature in a prototypical hybrid improper ferroelectric, that is, the (BiFeO3)/(NdFeO3) [abbreviated as (BFO)1/(NFO)1] 1:1 superlattice. In the high-temperature paraelectric phase, phonons having both polar and antipolar characters are found to exist, as a

result of a bilinear coupling between different cation motions, with these phonons having frequencies that are basically independent of temperature. In contrast, phonons having fluctuations of either in-phase or antiphase octahedral tiltings are soft in this high-temperature phase (with these two fluctuations being uncoupled), which results in their condensation below some critical temperature and the emergence of a low-temperature phase. In this latter low-temperature phase, trilinear energetic couplings between these two types of octahedral tiltings and Bi and Nd cations' motions lead to the appearance of a spontaneous polarization, consistent with the nature of hybrid improper ferroelectricity. These trilinear energetic couplings also yield an increase in the number of phonons possessing both polar and antipolar characters in the low-temperature phase, with most of these phonons softening when approaching the ferroelectric-to-paraelectric transition from below, as a result of the fact that they also exhibit antiferrodistortive features. The different temperature behaviors of polar modes at high versus low temperatures emphasize the uniqueness of hybrid improper ferroelectrics.

- "Rashba-like spin-orbit and strain effects in tetragonal PbTiO3," R. Arras, J. Gosteau, H. J. Zhao, C. Paillard, Y. Yang, and L. Bellaiche, Physical Review B 100, 174415 (2019).

We performed first-principles calculations of the spin-orbit effect appearing in the electronic structure of the well-known ferroelectric perovskite oxide PbTiO3 and analyzed the results within group-theory-derived models. We evidenced some non-negligible linear Rasbha spin splittings of the unoccupied p bands of Pb atoms and occupied p bands of oxygen atoms. Our calculations also show that a cubic spin splitting is present for the unoccupied dxy bands of Ti atoms. All these spin-orbit effects lead to complex spin textures reversible by switching the electric polarization, which could be used for future spinorbitronic applications. Our results also demonstrate how applying epitaxial strain could be envisaged to tune these properties by changing the relative energy of some of the bands or the magnitude of the linear/cubic coefficients describing the spin splitting.

DOI: 10.1103/PhysRevB.100.174415; published 11 November 2019

- "Designing multifunctionality via assembling dissimilar materials: Epitaxial AlN/ScN superlattices," Zhijun Jiang, Charles Paillard, David Vanderbilt, Hongjun Xiang and L. Bellaiche, Physical Review Letters 123, 096801 (2019).

First-principles calculations are performed to investigate the effect of epitaxial strain on energetic, structural, electrical, electronic, and optical properties of 1x1 AlN/ScN superlattices. This system is predicted to adopt four different strain regions exhibiting different properties, including optimization of various physical responses such as piezoelectricity, electro-optic and elasto-optic coefficients, and elasticity. Varying the strain between these four different regions also allows the creation of an electrical polarization in a nominally paraelectric material, as a result of a softening of the lowest optical mode, and even the control of its magnitude up to a giant value. Furthermore, it results in an electronic band gap that cannot only change its nature (direct vs indirect), but also cover a wide range of the electromagnetic spectrum from the blue, through the violet and near ultraviolet, to the middle ultraviolet. These findings thus point out the potential of assembling two different materials inside the same heterostructure to design multifunctionality and striking phenomena.

DOI: 10.1103/PhysRevLett.123.096801; published 28 August 2019

- "Photoinduced phase transitions in ferroelectrics," Charles Paillard, Engin Torun, Ludger Wirtz, Jorge Íñiguez and Laurent Bellaiche, Physical Review Letters 123, 087601 (2019).

Ferroic materials naturally exhibit a rich number of functionalities, which often arise from thermally, chemically, or mechanically induced symmetry breakings or phase transitions. Based on density functional calculations, we demonstrate here that light can drive phase transitions as well in ferroelectric materials such as the perovskite oxides lead titanate and barium titanate. Phonon analysis and total energy calculations reveal that the polarization tends to vanish under illumination, to favor the emergence of nonpolar phases, potentially antiferroelectric, and exhibiting a tilt of the oxygen octahedra. Strategies to tailor photoinduced phases based on phonon instabilities in the electronic ground state are also discussed.

DOI: 10.1103/PhysRevLett.123.087601; published 21 August 2019

III. List of Awards and Honors received

For the P.I.:

- Scientific Associate Investigator of the Australian FLEET center (ARC Centre of Excellence in Future Low-Energy Electronics Technologies) in 2019.

- SEC Faculty Achievement Award recipient in 2019.

- Elected a fellow of the Arkansas Research Alliance (ARA) in 2017.

For the postdoctoral fellows:

- Charles Paillard is a Professor at Ecole-Centrale-Supelec, France since 2019.

- ``Large-Scale Simulation of Thin Film Physics'' by Yousra Nahas, Sergei Prokhorenko and Laurent Bellaiche was included in the 2019 Coalition for Academic Scientific Computation (CASC) color brochure (which is the first time for any research group from the University of Arkansas).

For the graduate students:

- Third prize of the MicroEP IAB Poster and 3-min Presentation contests awarded to S. Omid Sayedaghaee at the Industrial Advisory Board of microEP; Fayetteville, Arkansas, October 02, 2017; ``The effect of time-dependent magnetic field on electrical polarization in bismuth ferrite,'' S. Omid Sayedaghaee, Sergey Prosandeev, Bin Xu, Charles Paillard, Laurent Bellaiche.

- First place of the MicroEP IAB Poster and 3-min Presentation contests awarded to S. Omid Sayedaghaee at the Industrial Advisory Board of microEP; Fayetteville, Arkansas, November 12, 2018; ``Novel Dynamical Magnetoelectric Effects in $BiFeO_3$: A Molecular Dynamics Study,'' S. Omid Sayedaghaee, Sergey Prosandeev, Bin Xu, Charles Paillard, Laurent Bellaiche.

- Temuujin Bayaraa, Master of Physics, Spring 2018, ``Properties of Epitaxial Sr0.5Ba0.5MnO3 Films from First principles.''

- Raymond Walter, Ph.D. of Physics, Spring 2019, ``Large-Scale Atomistic Simulations of Complex and Functional Properties of Ferroic Materials.''

For the undergraduate students:

- Robert D. Maurer scholarship awarded for ``outstanding Physics major" to Davis Campbell (Spring 2018).

- Student Undergraduate Research Fellowship (SURF) award from Arkansas Department of Higher Education awarded to Davis Campbell (Fall 2018).

- Honors College Travel Grant from the University of Arkansas awarded to Davis Campbell (Fall 2019).

- Davis Campbell, Honors Studies in Physics, Fall 2019, ``Finite Temperature Magnetic Properties of Rare-Earth Iron Garnets."

- Best Poster presented by a student at the 2020 Workshop on Fundamental Physics of Ferroelectrics and Related Materials; Silver Spring, MD, January 26-January 29, 2020; ``Finite Temperature Magnetic Properties of Rare Earth-Iron Garnets,'' Davis Campbell