First principles materials design of novel functional oxides

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We review our efforts to develop and implement robust computational approaches for exploring phase stability to facilitate the prediction-to-synthesis process of novel functional oxides. These efforts focus on a synergy between (i) electronic structure calculations for properties predictions, (ii) phenomenological/empirical methods for examining phase stability as related to both phase segregation and temperature-dependent transitions and (iii) experimental validation through synthesis and characterization. We illustrate this philosophy by examining an inaugural study that seeks to discover novel functional oxides with high piezoelectric responses. Our results show progress towards developing a framework through which solid solutions can be studied to predict materials with enhanced properties that can be synthesized and remain active under device relevant conditions.

Keywords: First principles; materials design and discovery; oxide solid solutions.

1. Introduction

The past two decades have seen an unprecedented explosion in the use of computational methods in scientific research ranging from drug discovery to the design of new materials for electrodes in Li-ion batteries. This growth has largely been fueled by a steady increase in computational resources coupled with new algorithms that take advantage of larger, faster, massively parallelized computers. In the arena of materials research, these advances have made it possible to use first principles, electronic structure methods to explore the fundamental properties of realistic materials, at the level of atoms and electrons.¹ Density functional theory (DFT) has had remarkable success for understanding how local interactions give rise to material responses, thus enabling the creation of design concepts for discovering new materials with enhanced behaviors. Moreover, once quantities relevant to macroscopic behaviors are known, high-throughput approaches that exploit the availability of massively parallel machines can be employed.^{2–10} In this way, a wealth of materials can be studied in a relatively short period of time. Data-mining strategies can then be used to extract the most promising materials based on data from crystal structure databases^{11,12} and first principles calculations. Excellent examples of this strategy include the Materials Project,¹³ the

Combinatorial Sciences and Materials Informatics Collaboratory (CoSMIC),¹⁴ the Automated Interactive Infrastructure and Database for Computational Science (AiiDA)¹⁵ and the Automatic Flow for Materials Discovery (AFLOW),¹⁶ which have shown remarkable progress in the discovery of novel materials for battery cathodes, oxide sensors and scintillators, to name a few.

Here, we review our progress towards developing an approach for designing and discovering novel functional oxides for piezoelectric applications. The focus is on the use of first principles calculations to predict materials with *enhanced properties that can be synthesized and remain active under device relevant conditions*. The working postulate is that a comprehensive understanding of stability with respect to oxide impurity phases or end member compounds can facilitate the prediction-to-synthesis process. This is one facet of the Materials Genome Initiative which seeks to accelerate materials discovery.¹⁷ The standard model has been to (1) use computation to predict materials properties and then (2) to attempt to grow the most promising materials. The potential for discovering materials in this manner is great. However, materials predicted by theory/computation are often either difficult to synthesize, requiring extreme conditions such as high temperatures and pressures, or are simply unstable and

Fig. 1. Prediction-to-synthesis triangle illustrating the three fundamental pillars of the computational materials discovery process: (i) Prediction of materials with desired properties, (ii) assessment of phase stability, both with regards to structural transitions and competing phases and (iii) experimental validation. This approach focuses on the computational examination of the relative stability of competing phases or impurities in order to shine a light on the feasibility of synthesizing a compound as well as its operability under specific conditions, which is often overlooked in the materials prediction process. Yet, routine assessment is necessary for discovering new materials.

thus segregate into secondary phases. Experimental feedback can be used to train the computational sets, but this is time consuming and can be quite computationally expensive. A third pillar of the prediction-to-synthesis triangle (see Fig. 1) should therefore include a theoretical assessment of the phase stability of predicted materials. Identification of the energetics of competing phases with different structures and stoichiometries will not only give a clear understanding of which structure is the ground state, but may give insight into which routes need to be taken to prepare the desired material. This has the potential for reducing the steps needed to get from properties prediction to experimental realization. Unfortunately, an understanding of the complex energy landscape of many materials remains elusive and is one of the great challenges in theoretical condensed matter physics today.¹⁸

In this paper, we present an example study which integrates properties prediction, experimental validation and phase stability to develop and build upon chemical concepts to design new materials with enhanced properties in the context of piezoelectrics. In particular, we will examine our efforts to map out the phase diagram of a disordered, perovskite oxide solid solution to identify regions of high piezoresponse that may be amenable to experimental synthesis. We will discuss the use and development of techniques to treat chemical disorder, relative stability of competing phases and ferroelectric phase transitions. Ultimately, we intend to present a framework through which solid solutions of oxides can be routinely studied to give experimentally realizable predictions.

2. Designer Solid Solutions

A useful strategy for creating high piezoresponse compounds borrows lessons from the prototypical piezoelectric $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT), a solid solution of the tetragonally distorted PbTiO_3 (PT) and the anti-ferrodistorted PbZrO_3 (PZ). The key to the success of PZT lies in the combination of perovskite compounds with two very distinct phases; leading to a composition-dependent region, the morphotropic phase boundary (MPB) at a concentration of roughly 50% PT/50% PZ. Here, the crystal structure undergoes a transition (mediated by a monoclinic phase¹⁹) between the macroscopic phases of the parent compounds²⁰ (i.e., the rhombohedral phase of the PZ-rich compositions and the tetragonal phase of the PT-rich compositions). In general, ferroelectric solid solutions near MPBs exhibit enhanced electromechanical responses when the parent compounds have high remnant polarizations.²¹ In this respect, the discovery of new MPB systems is an important step towards engineering high, electromechanical responses. The driving force of these high responses is often a result of competition between local strain or local bonding frustration and long range polar behavior.²²

As such, theoretical methods capable of probing local structure interactions are crucial for a precise understanding of the link between local structure and macroscopic properties. For example, using first principles studies we demonstrated that it is the cooperative off-centering of the *A*- and *B*-site ions that give rise to the MPB and large piezoelectric response of PZT.^{23,24} In particular, Pb displacements were observed to be extremely sensitive to the local *B*-site ordering, displacing away from the larger Zr cations and towards the smaller Ti ions, while conforming to the overall polarization. Hence, the relative concentration of Ti versus Zr critically defines the direction of the polarization; rotating from tetragonal to rhombohedral with increasing amounts of Zr cations. The challenge in developing new materials is finding combinations of *A*- and *B*-site cations that allow us to manipulate short-range behavior while maintaining the ferroelectric perovskite structure.

2.1. Properties prediction

In an attempt to design a novel lead-free piezoelectric based on the above chemical concept, we initially explored solid solutions of $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BZT) and $\text{La}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (LZT). Similar to PT, BZT has a super-tetragonal ground state,²⁵ while LZT is anti-ferroelectric²⁶ like PZ. Table 1 lists lattice constants and polarizations for the end member BZT and LZT bulk oxides. All calculations employed $2 \times 2 \times 2$ unit cells with rock salt ordering of Zn and Ti on the *B*-site. A tendency towards this ordering was recently demonstrated in BZT.²⁷ It should be noted that the DFT supercell calculations are the main bottleneck for obtaining the results discussed in this paper. A typical perovskite supercell self-consistent (scf) static calculation required approximately 7 minutes on

128 cores of a Cray XT system (i.e., Hopper at NERSC). A full relaxation of atomic coordinates and lattice constants may require a few 10s of scf steps. In principal, on a large cluster, jobs with different cation arrangements and compositions can be performed simultaneously. Nevertheless, a high-throughput study of the system described above may take on the order of a week to complete.

To search for a MPB in this compound we examined the polarization as a function of Bi versus La fraction assuming, to the best that it could have been maintained, rock salt ordering on the A-site (Fig. 2). This was done to reduce any artificial symmetry breaking due to A-site ordering. Subsequent calculations that mimic disorder revealed very little dependence on the A-site ordering. Here, we find that, for large fractions of La, the polarization remains very low, with marginal rhombohedral distortions. On the other hand for large fractions of Bi we observe a huge increase in the polarization with large tetragonal-like distortions and the absence of a monoclinic phase. In both cases, these results present unfavorable conditions for a high performance, room temperature ferroelectric. On the La-rich part of the phase diagram, the low polarizations may translate into extremely low transition temperatures as suggested by recent work by Grinberg and collaborators that used Landau theory to demonstrate that the magnitude of the polarization is correlated with the ferroelectric transition temperature.^{28,29} Conversely, the high polarizations in the Bi-rich region of the phase

diagram suggest that these compositions may not be ferroelectric as such large polarizations are often associated with loss in switchability and piezoelectric response as seen in compressively strained, epitaxial BiFeO₃.^{30–33}

To reduce the polarization of the Bi-rich region, and to improve solubility,³⁵ we examined the ternary phase diagram for solid solutions with PT. It is known that throughout the BZT–PT phase diagram the material remains tetragonal, with PT decreasing the magnitude of polarization. We found that in the BZT–LZT–PT ternary phase diagram, La plays two specific roles: (1) rotating the polarization away from the tetragonal direction towards the rhombohedral direction (for moderate amounts of LZT) and (2) reducing the magnitude of the polarization. Figure 3 depicts the magnitude and rotation of the polarization away from the tetragonal direction for the BZT–LZT–PT ternary solid solution. Here, we see a clear reduction in the total polarization with < 75% LZT compositions having reasonable polarizations. Furthermore, we note the presence of a monoclinic phase for PT concentrations between 25% and 50%.

2.2. Modeling solid solutions

Predicting the properties of oxide solid solutions requires the ability to find the ground state properties of a wide range of multi-atomic systems. The predicted ground state can be significantly influenced by the arrangement and compositional fraction of cations as well as the choice of unit cell or crystal structure. DFT supercell size constraints present additional limitations, particularly with regards to the treatment of disorder. To address the challenge of modeling disordered solid solutions, several approaches have been pursued to explore the rich landscape of structure- and composition-dependent properties. Atomic averaging approaches where individual atoms are viewed as either a combination of two or more atoms (virtual crystal approximation; VCA^{36,37}) or only seeing an average local environment (like the coherent potential approximation; CPA^{38,39}) have been successful in describing the properties of a number of systems.

In oxide ferroelectrics, such as the aforementioned PZT, these mean-field techniques often fail to capture the short-range local interactions that drive macroscopic phenomena such as polarization rotation and electromechanical responses.^{24,40,41} First principles methods can, however, be employed to parameterize larger unit cells or phenomenological models to study the effects of local variations in cation arrangements and composition. To date, these methods have given significant insight into the physical properties of a number of perovskite systems and when combined with molecular dynamics (MD) or Monte Carlo (MC) simulations can be used to explore temperature-dependent phase transitions and domain wall motion.^{42–47} Unfortunately, the extensive effort required to parameterize these potentials from large experimental or computational datasets has limited their widespread application.

Table 1. Lattice constant (a_0), c/a ratio and polarization for the end members of the ternary BZT–LZT–PT solid solution. Experimental values^{25,26} are listed in parentheses.

System	a_0 [Å]	c/a	P [C/m ²]
LZT	3.91 (3.95)	1.00 (1.00)	0.00 (0.00)
BZT	3.74 (3.82)	1.23 (1.211)	1.42 (1.50)
PT	3.85	1.05	0.79

Fig. 2. BZT–LZT solid solution polarization as a function of % Bi.³⁴

Fig. 3. (Color online) (Left) Atomic arrangement for a $3\text{Bi}(\text{Zn},\text{Ti})\text{O}_3-3\text{La}(\text{Zn},\text{Ti})\text{O}_3-2\text{PbTiO}_3$ supercell. Green and blue polyhedra denote Ti and Zn octahedra, respectively. Pink, red and black atoms represent Bi, La and Pb, respectively. (Right) BZT-LZT-PT ternary diagrams for (a) $|P|$ and (b) $P[001]$. For the $P[001]$ ternary diagram, the blue, purple and pink regions indicate areas that are tetragonal, monoclinic and rhombohedral, respectively. The green regions have little or no polarization. Black squares denote the compositions modeled. The dashed parallelogram represents the region of high stability. Adapted from Ref. 24. Copyright (2012) American Chemical Society.

An alternative is the special quasirandom structure (SQS)⁴⁸ method in which a supercell is selectively populated such that the short-ranged, geometric correlations approximate that of the random alloy. This approach has been widely used in the metals^{49–51} and semiconductors^{52,53} communities. Recently, using the SQS approach we examined the high temperature ($R3c$) and low temperature (Pm) phases of the KNbO_3 - NaNbO_3 (KNO-NNO) solid solution.⁵⁴ Similar to PZT, KNO-NNO shows a significant enhancement in piezoelectric response at a composition near $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)⁵⁵ and therefore has been considered to be an excellent starting structure for designing high-response, lead-free, electroceramics.^{56–58} Given the relative chemical similarities between K and Na, it is anticipated that these cations will be distributed randomly on the perovskite A -site. Figure 4 depicts the SQS and rock salt ordered structure (RSS) used to simulate KNN. In short, we find that the pair distribution functions (PDFs) generated with the SQS method were in excellent agreement with experimental PDFs for the two phases. This was in stark contrast with the RSS, which is often used to study these materials.⁵⁹ Analyses of the SQS polarization direction indicated that the macroscopic phase depends on the local, nearest-neighbor, Na-O interactions. These bond changes exhibit the most significant differences between the ground state $R3c$ and room temperature Pm phases; thus implicating Na interactions as the driving force for the observed electromechanical responses.

Theory and experiment have demonstrated that in materials with large size and charge differences on the B -site sub-lattice there may be a tendency towards B -cation ordering. This is often seen in Nb containing systems such as the relaxor systems $\text{Pb}(\text{Zn},\text{Nb})\text{O}_3$, $\text{Pb}(\text{Mg},\text{Nb})\text{O}_3$, and $\text{Pb}(\text{Sc},\text{Nb})\text{O}_3$.^{60–65} Such behavior was also observed in the $\text{Bi}(\text{Zn},\text{Nb})\text{O}_3$ -based systems.²⁷ For the BZT-LZT-SrTiO₃ (ST) solid solutions that we studied,⁶⁶ a comparison between the SQS

and RSS arrangements of Zn and Ti revealed that in the majority of instances the B -site RSS was the lowest energy structure. On the other, hand we found very little dependence of the total energy on the arrangement of cations on the A -site. Hence, for these systems and the BZT-LZT-PT systems we explored only the RSS arrangements.

Approaches like the SQS method and exploiting tendencies towards ordering are invaluable tools in the search and discovery of novel oxide solid solutions. Together, they facilitate the simulation of solid solutions, which would ordinarily require a large number of atoms, in manageable supercells; thereby allowing for realistic screening of materials and material properties.

Fig. 4. (Color online) (Left) The experimental (blue solid line) and theoretical reduced pair distribution functions for the high temperature $R3c$ (top) and low temperature Pm (bottom) phases of KNN. Rock salt (RSS) ordered and special quasirandom (SQS) structures are indicated by red dashed lines and black dash-dot lines, respectively. (Right) RSS and SQS atomic structures used to study the $R3c$ phase of KNN. Printed with permission from Ref. 54. Copyright (2014) American Physical Society.

2.3. Phase stability and experimental validation

Tremendous progress has been made in the field of modeling the thermodynamic stability of metal alloys.^{67–69} The combination of first principles calculations and thermodynamic/statistical methods with mean-field methods and the aforementioned SQS technique have allowed computational scientists to discern which metal alloys will form and thus may be suitable for synthesis.^{70–76} A pertinent example is the most recent work that investigated the electronic and structural properties of high entropy alloys.⁷⁷ Using enthalpies of formation computed directly from DFT and an ideal entropy of mixing model, they were able to build a model to identify all known single-phase alloys relative to those known not to form. Furthermore, they were able to extend this methodology to predict new high entropy alloys that had not been previously investigated.

To interrogate phase stability versus phase segregation into end member compounds, the Gibbs free energy, ΔG , upon mixing must be evaluated as:

$$\Delta G = \Delta H - T\Delta S. \quad (1)$$

ΔH , the enthalpy of mixing, can be computed directly from first principles calculations of the difference in total energy between the final solid solution or alloy and the end member compounds. T is temperature and ΔS is the change in entropy. In the case of these oxides configurational effects dominate, allowing us to use the entropy of mixing associated with an ideal random mixture, which can be evaluated as:

$$\Delta S = -k_B \sum_i x_i \ln x_i, \quad (2)$$

where x_i is the fraction of the i th end member compound in the solid solution or alloy and k_B is the Boltzmann constant.

We applied this approach to explore the phase stability of oxide solid solutions of BZT–LZT–PT³⁴ and BZT–LZT–ST.⁶⁶ Figure 5 depicts the Gibbs free energy evaluated with

the inclusion of configurational entropy as a function of BZT content for a binary solid solution of BZT–PT for different values of $k_B T$. To better understand the feasibility of synthesis, we compute the temperature (in meV) at which $\Delta G=0$ (Fig. 5 right). (This provides a simple approach to identifying which compositions are likely to form; in reality, equilibrium is determined by the choice of phase or phases that minimize the Gibbs free energy.) For the BZT–PT phase diagram, the $k_B T$ required to stabilize the solid solution is relatively small near the end members and increases to ~ 50 meV for a 50/50 composition. This phase stability range correlates well with a previous report on the $x\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3-y\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-z\text{PbTiO}_3$ perovskite ternary solid solution where mixed phases (i.e., phase segregation) were observed for BZT–PT compositions with greater than 40% BZT⁷⁸ and with other attempts to grow pure phases of BZT–PT.^{79,80}

Conversely, for the BZT–LZT solid solution (Fig. 5, right) we find that Bi is mostly insoluble in LZT and La also phase segregates in BZT, again, in agreement with experimental observations.³⁵ Our calculations further predict that for BZT–LZT, compositions between 37.5% and 62.5% LZT should be suitable for forming solid solutions. To test this theory, we attempted to make a 50% BZT/50% LZT solid solution. A stoichiometric mixture of Bi_2O_3 (Aldrich, 99.999%), La_2O_3 (Alfa Aesar, 99.99%), TiO_2 (Alfa Aesar, 99.9%) and ZnO (Alfa Aesar, 99.99%) were ground and pelletized using a cold press. The sample was fired at 750°C (5 h), 800°C (10 h), 850°C (10 h), and 900°C (10 h) in an alumina crucible with intermediate regrinding and pelletizing. Powder X-ray diffraction data were obtained with a PANalytical Empyrean diffractometer using $\text{Cu K}\alpha$ radiation, and were collected in Bragg–Brentano geometry on a flat plate holder. Figure 6 shows the X-ray crystal diffraction, XRD, spectra for a trial synthesis of BZT–LZT. The diffraction pattern shows peaks consistent with a cubic or pseudo-cubic perovskite structure. The pattern does not appear consistent with

Fig. 5. (Left) Gibbs free energy, ΔG for different temperatures (in units of $k_B T$ [meV]) as a function of %BZT for the BZT–PT phase diagram. (right) Temperature (in units of $k_B T$ [meV]) at which $\Delta G=0$ for the BZT–PT and BZT–LZT phase diagrams. The dotted line indicates $k_B T$ at room temperature, below which it is assumed that a solid solution will form.

potential non-bismuth containing perovskite phases such as $\text{La}_{2/3}\text{TiO}_3$ (ICSD 236451), LaTiO_3 (ICSD 63575) or reported monoclinic $\text{La}_2\text{ZnTiO}_6$ (ICSD 172755). Although some impurities, most likely excess Bi oxides, are present, these initial synthesis efforts signal promise for growing solid solutions of this phase. A more conclusive structural assignment will require further work to identify a phase pure region of the phase diagram.

An analysis of ΔG of the ternary BZT–LZT–PT solid solutions reveals two regions of stability. The first is for compositions with high PT content. Again, this is in good agreement with experimental results.^{79,80} The second region is a band between 37.5% and 67.5% BZT and < 67.5% PT concentrations (see Fig. 3(b)). This band overlays the monoclinic region as seen in Fig. 3(b) and may be a suitable region to explore for experimental synthesis efforts.

In their entirety, our initial theoretical and experimental attempts demonstrate that, similar to work on metal alloy systems, the configurational entropy is essential for identifying stable solid solutions which may be missed with a simple enthalpy of mixing calculation. Of course, other factors may contribute to phase stability. For example, the theoretical results presented here are relative to the end members of BZT and PT and exclude the possibility of PbO_2 (Scrutinyte) and Bi oxide compounds (e.g., Sillénite or Aurivillius forms), which are commonly observed in experiment.⁷⁸ Additionally, preparation conditions may play a role. Pure BZT requires high pressure synthesis (up to 6 GPa); thus, it stands to reason that solid solutions in the BZT–LZT–PT or BZT–LZT–ST phase diagrams with high BZT content may require similar synthesis conditions to be realized.

A final point to consider is temperature- (or pressure-) dependent phase transitions. Ferroelectric perovskites at high temperatures present a cubic, nonpolar phase. The lack of polarization in this phase renders them unusable as piezoelectrics at this temperature and thus the onset of this transition is critical to device performance. To elucidate the ferroelectric transition temperature, T_c , MC or MD simulations can be used to explore phase transition temperatures and the onset of ferroelectricity. However, such calculations,

Fig. 6. XRD spectra for the 50% BZT/50% LZT solid solution.

Fig. 7. (Color online) (Top) T_c versus P^2 for the BZT–LZT–PT solid solution (red circles). For comparison we plot the predicted polarizations versus the experimental T_c s for a range of Pb-based²⁸ and Bi-based²⁹ compounds. (bottom) Predicted T_c s as a function of LZT concentration for the BZT–LZT–PT solid solution. The dotted line indicates room temperature, while the red dashed line is a fit through the data emphasizing the correlation between T_c and LZT content.

directly from first principles results, are time consuming and require large unit cells or parameterized potentials. Using Landau theory, a clear correlation between experimental ferroelectric T_c s and computed polarizations, $T_c = \gamma P^2$, can be obtained.^{28,29} Using this relationship (with $\gamma = 870 \text{ K m}^4/\text{C}^2$) we approximated T_c s for our Bi-based compounds. Fig. 7 (top) depicts the predicted T_c versus the DFT computed polarization. For comparison, we plot the DFT computed polarization versus the experimental T_c s previously obtained for a set of Pb-based²⁸ and Bi-based²⁹ ferroelectric compounds. Remarkable agreement between the newly predicted results and the previous data can be seen. Interestingly, we also observe a strong dependence on La content (see Fig. 7, bottom). This is perhaps easily understood from Fig. 1 where we see that it is only after a considerable decrease in La content that the BZT–LZT solid solution recovers polarizations similar to that of the BZT end member. This indicates that La not only results in a rotation of polarization from [001] in these materials, but also restricts the total polarization by limiting the overall off-center displacements of the cations within the material; thereby being the driving force for tuning the ferroelectric transition temperature.

On the basis of our examination of the magnitude and orientation of the polarization as well as our predicted T_c and phase stability, we speculate that the region of the phase diagram bounded by $25\% \leq \text{PT} \leq 50\%$ and $50\% \leq \text{LZT} \leq 25\%$ should be the most likely compositions to find a high

response piezoelectric (see Fig. 3). In this region, we find suitably high polarizations ($0.71 \text{ C/m}^2 < P < 1.14 \text{ C/m}^2$) with moderate phase stability and appropriate $T_c > 500 \text{ K}$. Recent experimental efforts to grow regions of this ternary phase diagram further emphasize the importance of dialog between theory and experiment. In this regard, the evaluation of phase stability plays a crucial role in facilitating these interactions.

3. Conclusions and Outlook

The desire to accelerate materials discovery has propelled materials research in many new and fascinating directions. The need to understand the complex landscape of multi-component/multiphase materials not only presents new challenges for computational materials design, but it also provides new opportunities for the development of novel computational techniques. Data mining and high-throughput strategies have emphasized the value of electronic structure approaches for quickly predicting new materials. Methods like DFT have excelled at making accurate predictions of 0K ground state properties, while finite temperature properties may be explored using empirical potentials and MD and/or MC simulations. Similarly, thermodynamic models, like those that provide approximations for the entropy of mixing as an ideal random mixture, allow for the use of electronic structure energies to assess whether a material can be feasibly synthesized. These methods have been widely applied to metal alloy systems and, when coupled with techniques that can efficiently model disorder (e.g., the SQS approach) or search configurational space (e.g., genetic algorithms, simulated annealing, etc.), they provide a basis for discerning ground state materials properties. These approaches are now being applied to oxides and are yielding promising results. For instance, using SQS it is possible to gain insights into the driving mechanisms behind the transition between the low-temperature and high-temperature phases of the $(\text{K}_{1/2}\text{Na}_{1/2})\text{NbO}_3$ solid solution.⁵⁴ Additionally, predictions of phase stability point to potentially synthesizable regions of the $\text{Bi}(\text{Zn,Ti})\text{O}_3\text{--La}(\text{Zn,Ti})\text{O}_3\text{--PbTiO}_3$ phase diagram³⁴ (some of which have already been confirmed by experiment).

Ferroelectric oxides, such as the above-mentioned solid solutions, have a wide range of properties that involve coupling between electric, magnetic and lattice degrees of freedom. These behaviors are often influenced by environmental conditions such as temperature and pressure. While estimates of the temperature at which a material transforms from a high-temperature cubic, paraelectric phase to a ferroelectric, polar phase can be inferred based on the polarization of the ground state phase, further challenges remain. For instance many of these materials undergo a series of phase transitions as they cool down to 0K. Mapping out the pressure- and temperature-dependent phase diagram presents a unique and complex challenge, particularly for solid

solutions where it may not be trivial to parameterize empirical potentials or effective Hamiltonians. For now, these endeavors may be limited due to the computational demands. However, as computer processing power continues to increase and more efficient algorithms are developed, it may become possible in the near future to perform MC or MD simulations where the energy is evaluated directly from first principles calculations in reasonably sized supercells, thereby opening the door to mapping out the complex energy landscape of materials directly from electronic structure calculations.

More importantly the synergy between theory and experiment provides an opportunity for discovering new materials faster than in previous decades. Routine evaluations of phase stability and transition temperatures along with ground state properties signal an era of computational materials design of realistic, synthesizable materials that will remain active under device relevant conditions. This will reduce the cost needed to iterate through the prediction-to-synthesis cycle aiding in an accelerated materials discovery process, one that may take months rather than years.

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