

# Origin of Disorder Tolerance in Piezoelectric Materials and Design of Polar Systems

Handong Ling, Shyam S. Dwaraknath, and Kristin A. Persson\*



Cite This: <https://dx.doi.org/10.1021/acs.chemmater.9b04614>



Read Online

ACCESS |



Metrics & More

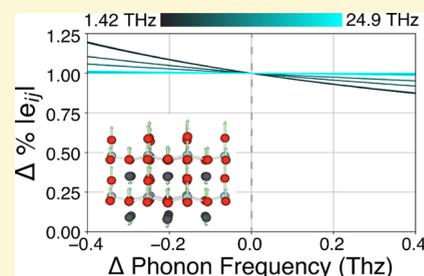


Article Recommendations



Supporting Information

**ABSTRACT:** Current high-performing piezoelectric materials are dominated by perovskites that rely on soft optical phonon modes stabilized by disorder near a morphotropic phase boundary and a unique resilience of the polar response to that disorder. To identify structural families with similar resilience, we develop a first-principles sensitivity analysis approach to determine the effect of disorder on the piezoelectric response for structures in the Materials Project database. In well-known piezoelectric systems, the lattice dynamics, rather than internal strain or dielectric, control the polar response. Additionally, multiple stable optical phonon modes are found to contribute to the piezoelectric response, providing a fingerprint for disorder tolerance. A multiple-phonon mode criterion is used to evaluate candidate materials for disorder-tolerant piezoelectric prototype systems. Five promising structures are altered through chemical substitution, generating potential MPB end points with large piezoelectric responses beyond perovskites including Akermanite  $\text{Sr}_{2x}\text{Ca}_{2-2x}\text{CoSi}_2\text{O}_7$ , which exhibits a nearly 20% increase in response at the 50% composition.



## INTRODUCTION

Piezoelectric materials are critical components in a wide variety of applications such as sensors, alarms, monitors, etc., resulting in a global piezoelectric device market that comprises an excess of US\$20 billion.<sup>4</sup> However, the most commonly used piezoelectric material,  $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  (PZT), warrants replacement due to the recent global regulation of lead as a hazardous element. PZT is a perovskite alloyed on the B-site near a morphotropic phase boundary (MPB) where the proximity to the MPB allows for a substantial change in the polarization direction with relatively small stress. These systems rely on a crystalline structure with soft optical phonon modes, stabilized through disorder or defects. Promising lead-free candidate systems to replace PZT include similar perovskite MPB systems,  $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$  (KNN), and  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT), which form solid solution disordered alloys near the relevant phase boundary. However, these alternatives do not yet exhibit the processing control, temperature stability, and piezoelectric efficiency to entirely replace PZT.<sup>18</sup> Improvements in KNN involve doping of the A and B perovskite sites with elements such as Li, Sb, and Ta, which have been shown to improve densification and the piezoelectric response.<sup>29,20,15,16</sup> In lead-free alternatives BNT and  $\text{BiFeO}_3$ , alloying additions of Mn and other transition-metal dopants have increased temperature and processing stability at the cost of piezoelectric response.<sup>30,24,31</sup> However, the magnitude of this decline is modest and still allows for their use as effective piezoelectric materials. The receptiveness of these materials to alloying and dopants near the morphotropic phase boundary is partly due to the inherent tolerance of their piezoelectric response to ionic disorder. As disorder is a

necessary component of modern piezoelectric systems, understanding its effect on the piezoelectric response is crucial to engineering lead-free piezoelectric systems.

Ab initio efforts also utilize disorder as a key parameter in designing piezoelectric materials. For example, investigations into the AlN system by Tholander et al.<sup>23</sup> have demonstrated the ability of disorder to enhance the piezoelectric response in wurtzite systems through alloying. For a wide variety of materials including perovskite, wurtzite, and zincblende structures, density functional theory has provided insight into the contributions to the increased piezoelectric response with changes in composition.<sup>22,1,10,9,7</sup> These approaches have focused on characterizing the Born effective charge and internal strain tensors to describe the change in piezoelectric response with respect to disorder while the phonon contributions are assumed constant. However, the lattice dynamics of the alloy, which are crucial to MPB systems,<sup>29</sup> are often not discussed, and the relative importance of Born effective charge and internal strain components has not been assessed in detail.

The Materials Project has developed a database of piezoelectric tensors comprising over 3000 compounds to aid in the search for lead-free piezoelectric materials.<sup>11</sup> However,

Received: November 7, 2019

Revised: March 11, 2020

Published: March 12, 2020

density functional theory approaches to calculating the piezoelectric tensor are limited in exploring disordered alloys as they are confined to finite unit cells with periodic boundary conditions. Indeed, a large number of promising predicted piezoelectric materials currently in the Materials Project are found to be specific orderings of materials naturally found with partially occupied cation or anion decorations as shown in Table 1.<sup>1</sup> It is unknown whether the ordered versions of these

**Table 1. Top 10 Calculated Piezoelectrics, as Ranked by the Largest Piezoelectric Modulus  $|e_{ij}|$ , from the Materials Project as of 2017 and PZT at the 50% Composition for Reference**

Formula (MP ID)	$ e_{ij} $ Max (C/m <sup>2</sup> )	Disorder Site
Pr <sub>3</sub> NF <sub>6</sub> (mp-33319)	83.84	Anion
SiO <sub>2</sub> (mp-557873)	63.03	
BaNiO <sub>3</sub> (mp-19241)	17.83	
Na <sub>2</sub> O (mp-776952)	14.23	
KBi <sub>2</sub> F <sub>7</sub> (mp-675634)	14.00	Cation
NaBiS <sub>2</sub> (mp-675531)	10.68	Cation
LiCo <sub>3</sub> OF <sub>5</sub> (mp-764144)	10.05	Anion
TiNO <sub>2</sub> (mp-676400)	8.86	Anion
SrHfO <sub>3</sub> (mp-13108)	8.73	
RbTaO <sub>3</sub> (mp-755018)	7.97	
PbTi <sub>0.5</sub> Zr <sub>0.5</sub> O <sub>3</sub> (mp-1079416)	6.87	Cation

experimentally observed disordered materials can be synthesized, and if so, whether disorder (which generally includes defective, alloyed, and doped materials) significantly affects the predicted piezoelectric response. In order to guide a broader structure and chemistry search for novel polar systems through computation, it is necessary to understand how disorder alters the piezoelectric response and how to identify systems in which the piezoelectric response is tolerant to disorder.

In this work, we develop a quantitative measure of the piezoelectric response to ionic disorder. We demonstrate its efficacy by examining the effect of perturbations on materials selected from the Materials Project's piezoelectric database. Specifically, we apply a statistical sensitivity analysis approach to explain the polar response to mild disorder in a structurally agnostic manner. This analysis can be applied to all piezoelectric tensors calculated in the framework set by Wu et al.,<sup>27</sup> which separates the piezoelectric response into an electronic component and ionic component. The ionic portion is then calculated from the Born effective charges (BECs), internal strain tensor (IST), and force constant matrix (FCM). From this analysis, we examine markers for the defect tolerance of modern alloy systems and apply this knowledge to identify potentially promising piezoelectric compounds that present both (i) strong intrinsic responses according to the *ab initio* calculations and (ii) a resilience under defect-level ionic disorder. We present these compounds as potential high-piezoelectric-response MPB prototype systems to be further explored, for example, through alloying as in the PZT system.

## COMPUTATIONAL PROCEDURES

The piezoelectric tensor is currently available for 3003 materials in the Materials Project, obtained from density functional perturbation theory (DFPT) calculations.<sup>2,3,8,11</sup> The first-principles calculations in this work are conducted with the Vienna Ab Initio Simulation Package (VASP)<sup>13,14</sup> using the PBE Generalized Gradient Approximation (GGA)<sup>19</sup> + U for

the exchange-correlation functional. An energy cutoff for the plane waves is set at 1000 eV with a *k*-point density of approximately 2000 per reciprocal atom (pra) for the piezoelectric DFPT calculations. The initial structural relaxations were conducted at an energy cutoff of 520 eV.

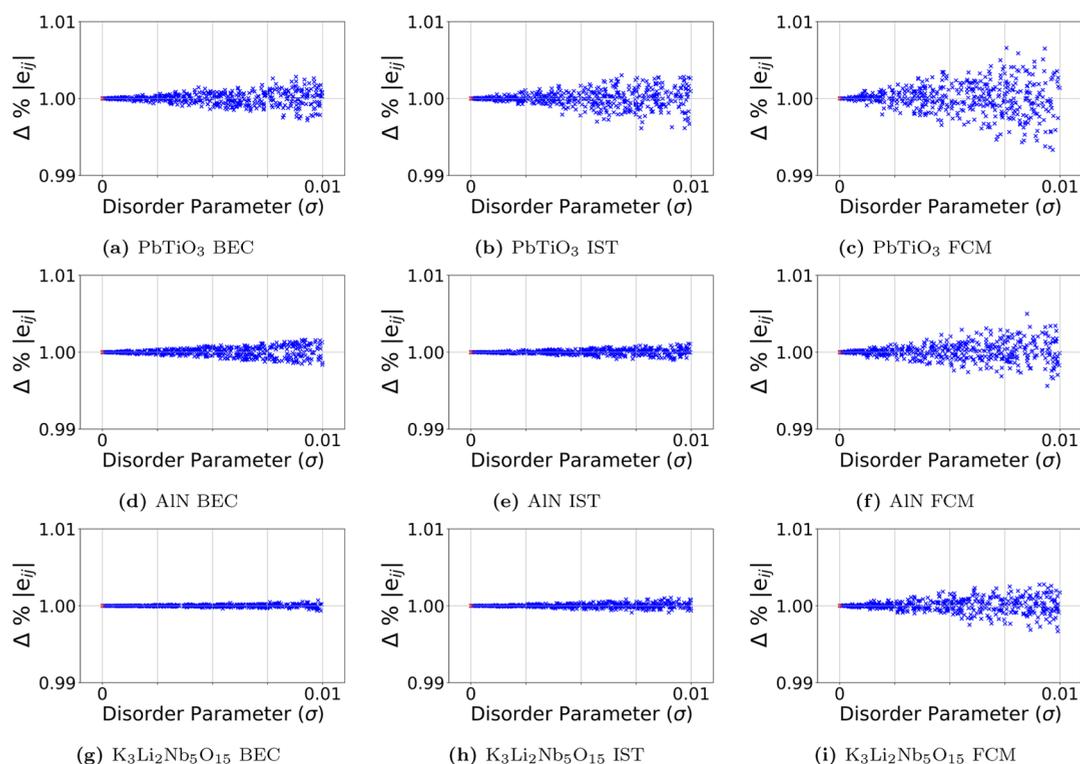
The piezoelectric tensor is calculated within density functional perturbation theory as

$$e_{aj} = \bar{e}_{ja} + \Omega_0^{-1} Z_{ma} (K^{-1})_{mn} \Lambda_{nj} \quad (1)$$

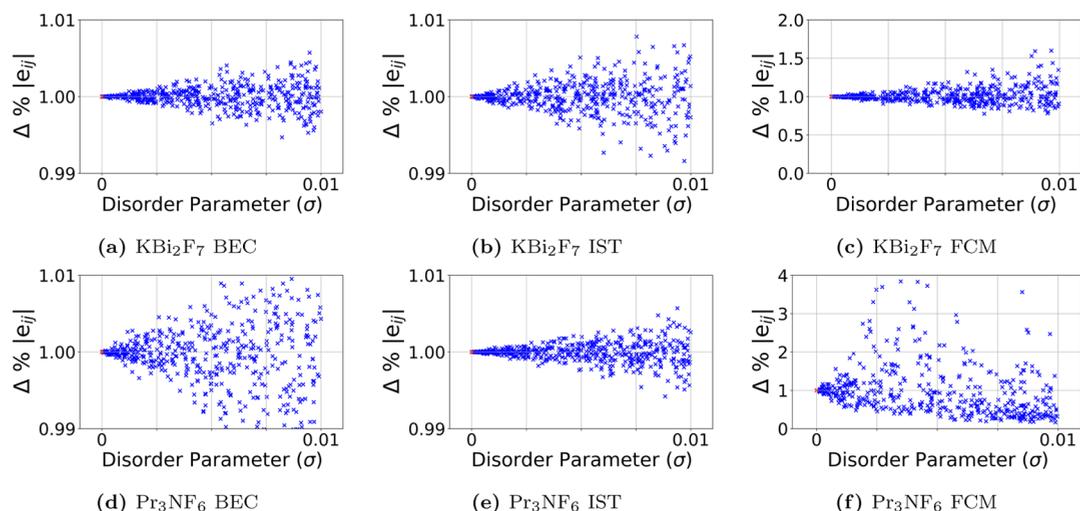
where  $e$  is the total piezoelectric tensor,  $\bar{e}$  is the electronic or clamped ion contribution to the piezoelectric tensor, and the remaining terms represent the relaxed ion contribution. The relaxed ion contribution consists of the unit cell volume  $\Omega_0$ , the Born effective charge  $Z$ , the force constant matrix  $K$ , and the internal strain tensor  $\Lambda$ .<sup>27</sup> We neglect the contribution of the electronic term,  $\bar{e}$ , in this study as it generally does not contribute significantly to the total piezoelectric tensor for the materials currently computed (see Figure S1). We consider the maximum piezoelectric modulus of the full tensor,  $|e_{ij}|$ , in this paper as the metric for the piezoelectric response.

Disorder is modeled by introducing stochastically distributed noise independently to each component of the DFPT-calculated piezoelectric tensor: the Born effective charge ( $\overline{BEC}$ ), internal strain tensor ( $\overline{IST}$ ), and force constant matrix ( $\overline{FCM}$ ). These perturbations are meant to approximate the local deviations in the dielectric, internal strain, and lattice dynamics of a material as would be introduced by random site disorder. While the dielectric and internal strain tensors can be thought of site property averages across the bulk disordered material, the force constants cannot be treated trivially. Disorder has been shown to induce broadening and splitting of phonon branches, not accounted for in our model.<sup>5,6</sup> However, studies on high-entropy alloys have determined that averaged force constants accurately reproduce phonon spectra at low frequency and long wavelengths.<sup>12</sup> In our model, only gamma point phonons are considered, and low-frequency phonon modes contribute most strongly to the piezoelectric response. We do not assume any relationship between the applied perturbations and thus randomly sample the effects on each component of the piezoelectric tensor over 500 unique perturbations. To ensure that the disorder is physically constrained, the appropriate symmetries of the tensors are preserved after the addition of noise to the DFPT-calculated  $\overline{BEC}$ ,  $\overline{IST}$ , and  $\overline{FCM}$ . In addition, sum rules for the Born effective charge tensors and force constant matrices are enforced as well as dynamic stability in the force constants. The procedure for generating the tensors, with correct symmetry and sum rules, is detailed in the Supporting Information, and the codebase for this analysis is available online through Pymatgen in the site\_symmetries and piezo\_sensitivity modules. Analysis of the dynamical matrix is performed with the Phonopy package.<sup>25</sup>

The magnitude of disorder is controlled by scaling the generated noise tensors to the maximum value of the associated DFPT-calculated tensors ( $\overline{BEC}$ ,  $\overline{IST}$ , and  $\overline{FCM}$ ), then multiplying by a scalar, denominated the disorder parameter:  $\sigma$ . Subsequently, the noise tensors are added to their respective DFPT-calculated piezoelectric tensors. We choose a maximum disorder parameter of 0.01 to approximate a 1% change in the site properties. We emphasize that  $\sigma$  does not represent a formal order parameter but is rather constructed to understand the sensitivity of the piezoelectric



**Figure 1.** Effect of  $\sigma$  on the maximum modulus of the piezoelectric tensor when applied to the Born effective charges (a,d,g), internal strain tensors (b,e,h), and force constant matrices (c,f,i) for  $\text{PbTi}_{0.5}\text{Zr}_{0.5}\text{O}_3$ , AlN, and  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ .



**Figure 2.** Effect of  $\sigma$  on the maximum piezoelectric tensor component when applied to the BEC, IST, and FCM for  $\text{Pr}_3\text{NF}_6$  and  $\text{KBi}_2\text{F}_7$ .

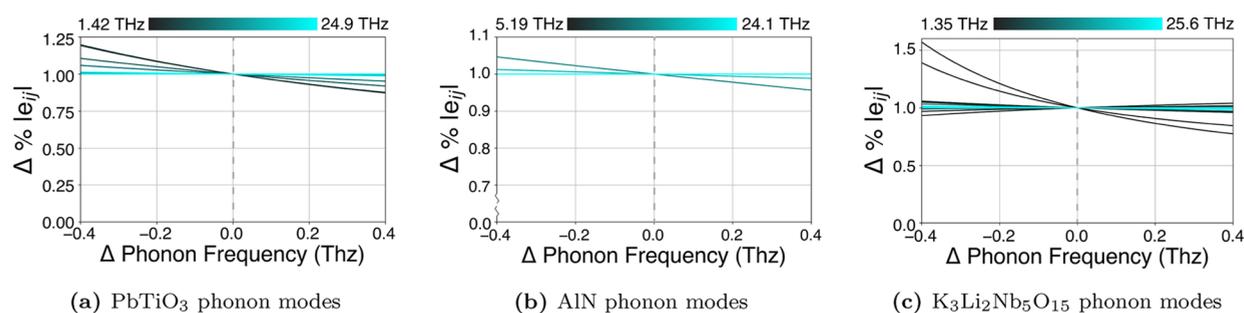
response to the three individual components of the relaxed ion contribution.

Chemical substitutions were attempted on structures tolerant to disorder to generate new piezoelectric compounds. Substitutions on the structural prototypes are performed based on similar atomic size, common oxidation states, and valence states. At least 4 cation substitutions were performed on each structural prototype, and the highest performing compound calculated is included in Table 2.

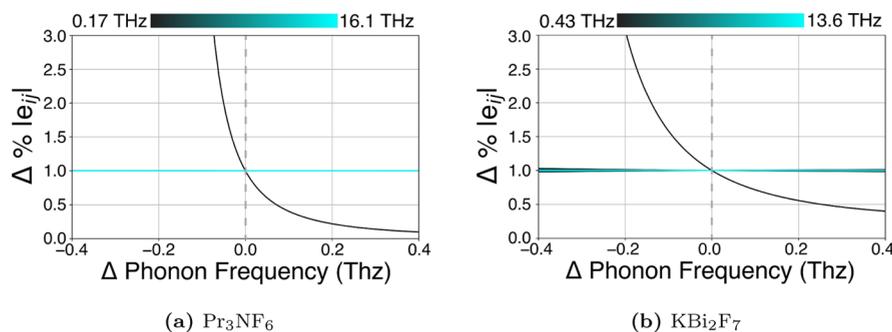
## RESULTS AND DISCUSSION

We first apply the disorder sensitivity analysis to piezoelectric systems that are known to retain strong piezoelectric responses upon ionic disorder to demonstrate the empirical efficacy of

our disorder model. For these disorder-tolerant systems, we choose perovskite  $\text{PbTiO}_3$ , wurtzite AlN, and  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  in the tungsten bronze structure.  $\text{PbTiO}_3$  represents the end point composition of PZT, AlN has been shown to exhibit an increased piezoelectric response through alloying, and several alloys in the tungsten bronze structure are known to be strong piezoelectrics.<sup>23,18,28,17</sup> The same analysis is then applied to a select number of top, predicted polar candidate materials from the Materials Project (see Table 1). We then identify the low-lying optical phonon modes that are primarily responsible for the large piezoelectric response to explain the mechanism of disorder tolerance in these materials (Figure 4). Lattice dynamic properties are then used to identify descriptors and design metrics for defect tolerance in polar structures, such as



**Figure 3.** Optical phonon frequencies of (a)  $\text{PbTiO}_3$ , (b)  $\text{AlN}$ , and (c)  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$  are varied independently to determine the effect of each individual mode on the piezoelectric tensor.



**Figure 4.** Optical phonon frequencies of (a)  $\text{Pr}_3\text{NF}_6$  and (b)  $\text{KBi}_2\text{F}_7$  are varied independently to determine the effect of each individual mode on the piezoelectric tensor.

perovskites, which retain a strong piezoelectric response under cation/anion disorder. The design metric is subsequently applied to search for new, disorder-tolerant piezoelectric systems, which may be optimized to further increase their piezoelectric response through alloying.

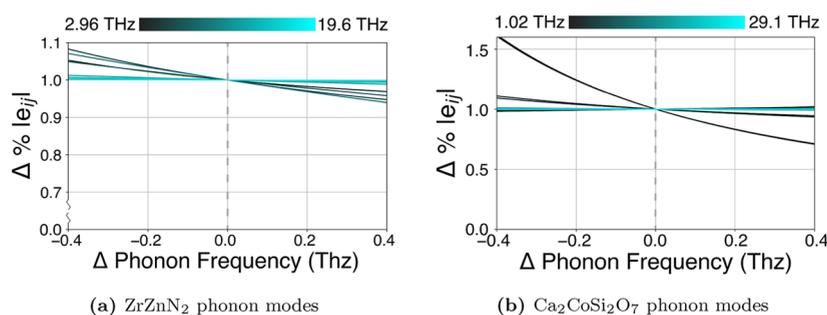
**Origin of Disorder Tolerance in Current Piezoelectric Materials.** Figure 1 shows the effect of perturbations scaled by the disorder parameter,  $\sigma$ , on the modulus of the piezoelectric tensor. These perturbations are applied independently to the DFPT-calculated Born effective charges, internal strain tensors, and force constant matrices. A few observations can be made from the results in Figure 1: first, the random noise imposed on the each component has an overall low impact, approximately within a percent, on the piezoelectric response. Second, the disorder parameter has an almost equal probability of increasing or decreasing the piezoelectric response, as evidenced by the symmetric cone around the original response from the perfectly ordered material. Therefore, we find that disorder on these properties does not significantly or systematically affect the piezoelectric responses of these materials. This resilience to disorder is consistent with the experimental performances of these materials.<sup>32</sup>

Extending to novel systems, we now apply our disorder model to two of the Materials Project's top piezoelectric candidates that exhibit partial occupancies in their as-synthesized form,  $\text{KBi}_2\text{F}_7$  and  $\text{Pr}_3\text{NF}_6$ , in order to determine their sensitivity to disorder. The results are shown in Figure 2. Similar to the known piezoelectrics, when  $\overline{\text{BEC}}$  and  $\overline{\text{IST}}$  are altered by  $\sigma$ , the piezoelectric modulus shows a nearly random spread around the original response with low amplitude, demonstrating a modest effect on the polar response. However, the piezoelectric responses of  $\text{KBi}_2\text{F}_7$  and  $\text{Pr}_3\text{NF}_6$  show large variation when  $\sigma$  is applied to  $\overline{\text{FCM}}$ . In the case of  $\text{Pr}_3\text{NF}_6$ , disorder tends to show a decline in the piezoelectric response.

We therefore note the ability of the force constants, rather than the Born effective charges and internal strain properties, to cause large variation in the piezoelectric response with respect to small perturbations.

To confirm and further examine this apparent sensitivity to disorder, DFPT piezoelectric calculations on varied cation and anion orderings (as found experimentally) of  $\text{Pr}_3\text{NF}_6$  and  $\text{KBi}_2\text{F}_7$  were conducted.<sup>21,26</sup> The responses for different orderings are presented in Table S1. The piezoelectric response is shown to degrade dramatically as the ionic ordering is changed. The sensitivity of the piezoelectric response to the disorder parameter and the degradation of the response seen in alternative orderings indicate that these candidate materials would not be suitable for experimental synthesis. On the other hand, changes to the ordering on the B-site of PZT at the 50% composition only cause a variation of 3% in the maximum piezoelectric response in DFPT calculations (also shown in Table S1).

We explore the origin of this sensitivity to disorder by examining the optical phonon modes that contribute to the piezoelectric response by diagonalizing the dynamical matrices obtained from the DFPT-generated force constants. Disorder is known to broaden the distribution of phonon frequencies from the ordered lattice phonon spectra, which is consistent with the effects of our disorder parameter on the phonon spectra shown in Figure S4.<sup>12,5</sup> We examine the effects of this broadening on the piezoelectric response by individually altering the phonon frequencies of the disorder-tolerant materials in Figure 3.<sup>2</sup> For these perovskite, wurtzite, and tungsten bronze systems, we find that varying the frequency of any individual phonon mode results in a modest decrease in the piezoelectric response, consistent with the trends in Figure 1. We also observe a multiplicity of stable optical phonon modes contributing to the piezoelectric response. In these



**Figure 5.** Responses of the maximum piezoelectric component with respect to variations in optical phonon frequencies of (a)  $\text{ZrZnN}_2$  and (b)  $\text{Ca}_2\text{CoSi}_2\text{O}_7$  suggest similar behavior to those of the disorder-tolerant  $\text{PbTiO}_3$ , KNN, and BNT perovskites, as well as AlN and  $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ .

**Table 2.** Changes in Piezoelectric Response of the Identified Disorder-Tolerant Structural Prototypes Are Shown along with the Energies above Hull before and after the Cation Replacement.<sup>a</sup>

Materials Project Prototype (MP ID)	Prototype $ e_{ij} $ Max ( $\text{C}/\text{m}^2$ )	Energy above Hull (eV)	Substitutional Compound (MP ID)	Substitutional Compound $ e_{ij} $ Max ( $\text{C}/\text{m}^2$ )	Energy Above Hull (eV)	% Change in Piezoelectric Response
$\text{NbCl}_2\text{O}$ (mp-1025567)	3.78	0.0	$\text{VCl}_2\text{O}$ (mp-690526)	3.05	0.091	-19.3%
$\text{ZrZnN}_2$ (mp-1014244)	2.85	0.0	$\text{ZrHfN}_2$ (mp-1224247)	2.51	0.0	-11.8%
GeTe (mp-938)	3.92	0.0	GeSe (N/A)	2.93	0.0	-25.2%
$\text{WOF}_4$ (mp-765135)	2.81	0.0	$\text{MoOF}_4$ (N/A)	1.23	0.151	-56.2%
$\text{Ca}_2\text{CoSi}_2\text{O}_7$ (mp-18786)	3.85	0.018	$\text{SrCaCoSi}_2\text{O}_7$ (N/A)	4.78	0.039	+19.2%

<sup>a</sup>For these structures, a large piezoelectric response is still accessible after cation substitution. N/A in the MP ID field identifies a structure not previously calculated in the Materials Project.

systems, disorder-induced broadening of an individual mode does not significantly alter the piezoelectric response as an individual mode does not dominate the piezoelectric response. In addition, frequency broadening of a single mode may be compensated for by variations in other contributing modes. These structural families exhibit significant piezoelectric responses, favorable responses to alloying, and large chemical diversity, and in these materials, we emphasize the identification of not one, but several stable optical modes in these systems that are associated with a resilience to  $\sigma$  in these materials. Similar trends were found in the DFPT-calculated structures of  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  and  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (Figure S3). The existence of several modes with a significant impact on the polar response is a signature of these highly symmetric perovskite structures and likely a key reason for its dominance among polar materials.

However, in  $\text{Pr}_3\text{NF}_6$  and  $\text{KBi}_2\text{F}_7$ , which show large variation in the piezoelectric response with  $\sigma$ , we find that a single soft optical mode is responsible for the large response of the perfectly ordered lattice (see Figure 4). The frequencies of these phonon modes are the lowest in each material at 0.171 THz in  $\text{Pr}_3\text{NF}_6$  and 0.433 THz in  $\text{KBi}_2\text{F}_7$ . Conversely, when the frequencies of other optical modes are varied, little to no change in the maximum piezoelectric modulus occurs. DFPT calculations (Table S1) confirm that this single soft phonon mode is highly sensitive to ionic ordering and controls the degradation of piezoelectric responses of these materials. Orderings for other experimentally disordered materials in Table 1 ( $\text{NaBiS}_2$  and  $\text{TlNO}_2$  shown in Table S1) also support this multiple-stable-phonon criterion for disorder tolerance.

In summary, the Born effective charge and internal strain tensor are found to contribute relatively little to the piezoelectric response when perturbed compared to the force constant matrix. We posit that a piezoelectric response that involves several stable phonon modes is much more likely to exhibit disorder tolerance, as compared to those involving a

singular soft mode as found in  $\text{KBi}_2\text{F}_7$  and  $\text{Pr}_3\text{NF}_6$ . We note that both  $\text{KBi}_2\text{F}_7$  and  $\text{Pr}_3\text{NF}_6$  are observed experimentally with partial occupancies on their cation/anion lattices, so it is highly unlikely that they exhibit any substantial piezoelectric response in their as-synthesized forms as indicated by our sensitivity model and supported by DFPT calculations of varied ionic orderings.

**New Defect-Tolerant Piezoelectrics.** From the results in the previous section, we observe a strong correlation between a “disorder-tolerant” piezoelectric response and the existence of several optical modes responsible for the favorable piezoelectric distortion. Using this phonon criterion, we present five structural prototypes from the Materials Project’s 100 highest response piezoelectric materials that show promise as potential MPB systems. These identified prototype structures are hypothesized to retain large piezoelectric responses after alloying. For two of these materials,  $\text{ZrZnN}_2$  and  $\text{Ca}_2\text{CoSi}_2\text{O}_7$ , we show the effect of the broadening of phonon frequencies on the piezoelectric response in Figure 5 to demonstrate the same retention of the polar response as known piezoelectrics under mild disorder (Figure 3). These five prototype structures are outside of the perovskite family and include layered configurations (e.g.,  $\text{NbCl}_2\text{O}$  and  $\text{ZrZnN}_2$ ), rocksalt-like structures (GeTe), and Akermanite ( $\text{Ca}_2\text{CoSi}_2\text{O}_7$ ).

For the identified prototype systems, explicit ionic substitutions were explored to determine if the hypothesized disorder tolerance allows for new chemistries to be discovered from these structural starting points. Several substitutions based on reasonable chemical rules such as ionic size and charge (see Computational Procedures for details) were attempted on the prototype cation sites. The structures were then relaxed, and DFPT was utilized to obtain the full piezoelectric tensors. A summary of the results and the chemical substitutions, which retain or increase the piezoelectric response of the original compound, are shown in Table 2. In addition to the maximum piezoelectric response for both

prototype compounds as well as the substituted material, Table 2 includes information on the change in piezoelectric response and energy above hull.<sup>3</sup>

The piezoelectric tensors of the substituted materials in Table 2 were not previously calculated and are all within the top 10% of the Materials Project database in piezoelectric response.<sup>11</sup> This suggests that the cation substituted compounds may be promising candidates for novel piezoelectric materials. However, these materials are also potential end points of alloy systems. Each structural prototype will require further investigation with respect to various dopants, orderings, and structural distortions to optimize the piezoelectric response as in the perovskite system. The SrCaCoSi<sub>2</sub>O<sub>7</sub> system is given as an example of substitution that predicts an increase in the piezoelectric response, highlighting the opportunity to further explore these disorder-tolerant systems through alloying. The nearly 20% increase in piezoelectric response is attributed to softening of specific optical phonons associated with the Sr atoms moving out of phase and pairs of Si tetrahedra flexing or rotating to accommodate this motion. We hypothesize that the Sr<sub>2x</sub>Ca<sub>2-2x</sub>CoSi<sub>2</sub>O<sub>7</sub> system and many others of these disorder-tolerant systems may be further investigated to explore the existence of an MPB and hence an even greater piezoelectric response.

## CONCLUSIONS

Polar functional materials are dominated by the perovskite structure family, including the leading commercial piezoelectric, PZT. To diversify our portfolio of possible polar functional materials and aid in the design of novel lead-free piezoelectric materials, the Materials Project has recently launched a large search for novel systems beyond the perovskite family. Interestingly, a larger-than-expected number of the resulting predicted high-performing piezoelectrics exhibited a specific ionic ordering, while the as-synthesized materials presented partial occupancies. A commercially viable piezoelectric material is likely to employ alloying as a tuning strategy and hence necessitates retention of its polar response under ionic disorder. To identify such disorder-tolerant polar prototype structures and systems, we develop a statistical sensitivity analysis on the first-principles computed piezoelectric tensor.

Performing the analysis on known high-performing materials (PbTiO<sub>3</sub>, KNN, BNT, AlN, and K<sub>3</sub>Li<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub>) provides insight into the robustness of the perovskite system, which exhibits a large piezoelectric response under ionic disorder and alloying. While the dielectric and internal strain properties were found to react relatively weakly to the disorder parameter,  $\sigma$ , perturbations to the lattice dynamics are found to heavily control the polar response. Disorder-induced broadening of phonon mode frequencies, which contribute to the piezoelectric response, controls this behavior. Indeed, multiple optical modes in known piezoelectric perovskite systems each contribute significantly to the piezoelectric response, signaling a tolerance to disorder. In contrast, many of the novel computed materials, which were predicted to exhibit a large piezoelectric response for a particular ionic ordering, were found to be highly sensitive to even mild ionic disorder. In these materials, a single soft optical phonon mode was responsible for the large polar response. Examples include Pr<sub>3</sub>NF<sub>6</sub> and KBi<sub>2</sub>F<sub>7</sub>, and hence, these compounds are excluded as suitable candidates due to the strong disorder-induced degradation in the piezoelectric effect. We hope that this

analysis of lattice dynamics in piezoelectric materials will continue to guide the search for lead-free MPB systems.

The insights gained were used to filter systems in the Materials Project piezoelectric collection for similar disorder tolerance to the perovskite family. Five structural prototypes were identified. The prototypes were used for explicit cation substitutions, and the best-performing chemical systems are presented as possible starting points for future alloying strategies. Each of these novel compounds is predicted to exhibit disorder resilience originating from multiple stable optical phonons contributing to the polar response. In addition, the maximum piezoelectric moduli of these materials are within the top 10% of those in the Materials Project. We offer a screening strategy as well as new structural systems to the community in an effort to contribute to the search for novel environmentally friendly piezoelectrics.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.9b04614>.

Symmetry constraint procedures; MP data on ionic and electronic contributions; disorder data for KNN and BNT; disorder parameter broadening of phonon spectra; phonon mode visualization for PZT; ordering data for experimentally disordered materials; diagram of piezoelectric tensor symmetry algorithm (ZIP)

## AUTHOR INFORMATION

### Corresponding Author

Kristin A. Persson – *Materials Science and Engineering Department, University of California Berkeley, Berkeley, California 94704, United States*; [orcid.org/0000-0003-2495-5509](https://orcid.org/0000-0003-2495-5509); Email: [kapersson@lbl.gov](mailto:kapersson@lbl.gov)

### Authors

Handong Ling – *Materials Science and Engineering Department, University of California Berkeley, Berkeley, California 94704, United States*; [orcid.org/0000-0002-7776-9913](https://orcid.org/0000-0002-7776-9913)

Shyam S. Dwaraknath – *Energy Storage & Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States*; [orcid.org/0000-0003-0289-2607](https://orcid.org/0000-0003-0289-2607)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acs.chemmater.9b04614>

### Author Contributions

K.A.P. and S.S.D. conceived the project, and H.L. conducted the analysis. K.A.P. and S.S.D. supervised the project, and all authors discussed the results and contributed to the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was primarily supported by the Center for Next Generation Materials by Design, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-AC02-05CH11231. Data infrastructure, algorithms, and software development was supported by the Materials Project, funded

by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231:Materials Project program KC23MP. Computational resources were provided by the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the DOE under Contract No. DE-AC02-05CH11231.

## ■ ADDITIONAL NOTES

<sup>1</sup>These artificially ordered compounds are approximations of disordered ionic systems due to the limitation of ab initio simulations, which require exactly specified atomic elements and positions.

<sup>2</sup>0.4 THz is chosen from the difference between the softened phonon mode in PZT compared to PbTiO<sub>3</sub>, which correlates to the largest change in piezoelectric effect (seen in Figure S4).

<sup>3</sup>Energy above hull refers to the energy of decomposition of a material into the most stable compounds at a specific composition. An energy above hull of zero corresponds to the lowest energy structure at the composition with respect to decomposition to referenced compounds.

## ■ REFERENCES

- (1) Akgenç, B.; et al. First - principles calculations on stability and mechanical properties of various ABO<sub>3</sub> and their alloys. *Mater. Chem. Phys.* **2018**, *205*, 315–324.
- (2) Baroni, S.; et al. Green's-Function Approach to Linear Response in Solids. *Phys. Rev. Lett.* **1987**, *58*, 1861–1864.
- (3) Baroni, S.; et al. Phonons and related crystal properties from density-functional perturbation theory. *Rev. Mod. Phys.* **2001**, *73*, 515.
- (4) Bell, A. J.; Deubzer, O. Lead-free piezoelectrics—The environmental and regulatory issues. *MRS Bull.* **2018**, *43*, 581–587.
- (5) Bouchbinder, E.; Lerner, E. *Universal disorder-induced broadening of phonon bands : from disordered lattices to glasses Universal disorder-induced broadening of phonon bands : from disordered lattices to glasses*; In *New Journal of Physics*, **2018**, pp. 0–16.
- (6) Bungaro, C.; Rabe, K. M. Lattice instabilities of PbZrO<sub>3</sub> PbTiO<sub>3</sub> superlattices from first principles. *Phys. Rev. B* **2002**, *65*, 224106.
- (7) Daoust, P.; Desjardins, P.; Masut, R. A.; Gosselin, V.; Côté, M. Ab initio piezoelectric properties of Al<sub>0.5</sub>Sc<sub>0.5</sub>N : Impact of alloy configuration on the d<sub>33,f</sub> piezoelectric strain coefficient. *Phys. Rev. Mater.* **2017**, 055402.
- (8) Gonze, X. Adiabatic density-functional perturbation theory. *Phys. Rev. A* **1995**, *52*, 1096.
- (9) Hirata, K.; et al. First-Principles Study of Piezoelectric Properties and Bonding Analysis in ( Mg , X , Al ) N Solid Solutions ( X = Nb , Ti , Zr , Hf ). *ACS Omega* **2019**, *4*, 15081–15086.
- (10) Hultman, L.; et al. Ab initio calculations and experimental study of piezoelectric YxIn<sub>1-x</sub>N thin films deposited using reactive magnetron sputter epitaxy. *Acta Mater.* **2016**, *105*, 199–206.
- (11) de Jong, M.; et al. A database to enable discovery and design of piezoelectric materials. *Sci. Data* **2015**, *2*, 150053.
- (12) Körmann, F.; et al. Phonon broadening in high entropy alloys. *npj Comput. Mater.* **2017**, *36*.
- (13) Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558–561.
- (14) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.
- (15) Li, J.-F.; et al. (K, Na) NbO<sub>3</sub>-based lead-free piezoceramics: Fundamental aspects, processing technologies, and remaining challenges. *J. Am. Ceram. Soc.* **2013**, *96*, 3677–3696.
- (16) Ming, B. Q.; et al. Piezoelectric properties of (Li, Sb, Ta) modified (Na,K) NbO<sub>3</sub> leadfree ceramics. *J. Appl. Phys.* **2007**, *101*, No. 054103.
- (17) Neurgaonkar, R. R.; et al. Piezoelectricity in tungsten bronze crystals. *Ferroelectrics* **1994**, *160*, 265–276.
- (18) Panda, P. K.; Sahoo, B. PZT to lead free piezo ceramics: A review. *Ferroelectrics* **2015**, *474*, 128–143.
- (19) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (20) Saito, Y.; et al. Lead-free piezoceramics. *Nature* **2004**, *432*, 84–84.
- (21) Soubeyroux, J.; Reau, J.; Matar, S.; Villeneuve, G.; Hagenmuller, P. ETUDE PAR DIFFRACTION NEUTRONIQUE DES SOLUTIONS SOLIDES K<sub>1-x</sub>Bi<sub>x</sub>F<sub>1+2x</sub> ET Rb<sub>1-x</sub>Bi<sub>x</sub>F<sub>1+2x</sub>. *Solid State Ionics* **1982**, *6*, 103–111.
- (22) Tan, Z.; et al. Intrinsic origin of enhanced piezoelectricity in alkali niobate - based lead - free ceramics. *J. Am. Ceram. Soc.* **2019**, *102*, S262–S270.
- (23) Tholander, C.; et al. Large piezoelectric response of quaternary wurtzite nitride alloys and its physical origin from first principles. *Phys. Rev* **2015**, 174119.
- (24) Peng, P.; et al. Enhanced ferroelectric properties and thermal stability of Mn-doped 0.96(Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub>-0.04BiAlO<sub>3</sub> ceramics. *J. Am. Ceram. Soc.* **2017**, 1030–1036.
- (25) Togo, A.; Tanaka, I. First principles phonon calculations in materials science. *Scr. Mater.* **2015**, *108*, 1–5.
- (26) Vogt, T.; Schweda, E.; Laval, J. P.; Frit, B. Neutron Powder Investigation of Praseodymium and Cerium Nitride fluoride solid solutions. *J. Solid State Chem.* **1989**, *83*, 324–331.
- (27) Wu, X.; Vanderbilt, D.; Hamann, D. R. Systematic treatment of displacements, strains, and electric fields in densityfunctional perturbation theory. *Phys. Rev. B* **2005**, *72*, No. 035105.
- (28) Xin, J.; Zheng, Y.; Shi, E. Piezoelectricity of zinc-blende and wurtzite structure binary compounds. *Appl. Phys. Lett.* **2007**, *91*, 112902.
- (29) Xing, J.; et al. Properties and structures of nonstoichiometric (K, Na)NbO<sub>3</sub>-based leadfree ceramics. *J. Am. Ceram. Soc.* **2018**, *101*, 1632–1645.
- (30) Zhang, S.; Xia, R.; ShROUT, T. R. Modified (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> based lead-free piezoelectrics with broad temperature usage range. *Appl. Phys. Lett.* **2007**, *91*, 132913.
- (31) Zheng, T.; Wu, J. Effects of site engineering and doped element types on piezoelectric and dielectric properties of bismuth ferrite lead-free ceramics. *J. Mater. Chem. C* **2015**, 11326–11334.
- (32) Zheng, T.; et al. Recent development in leadfree perovskite piezoelectric bulk materials. *Prog. Mater. Sci.* **2018**, *98*, 552–624.