

Ab Initio Design of Perovskite Alloys with Predetermined Properties: The Case of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$

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A first-principles derived approach is combined with the inverse Monte Carlo technique to determine the atomic orderings leading to prefixed properties in $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ perovskite alloy. We find that some arrangements between Sc and Nb atoms result in drastic changes with respect to the disordered material, including ground states of new symmetries, large enhancement of electromechanical responses, and considerable shift of the Curie temperature. We discuss the microscopic mechanisms responsible for these unusual effects.

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Perovskite alloys with the general form $(A'A''\dots)(B'B''\dots)\text{O}_3$ are of great technological interest because of their large piezoelectric and dielectric responses [1]. Examples of their applications are piezoelectric transducers and actuators, nonvolatile ferroelectric memories, and microelectronic devices. Interestingly, little is known and understood about the microscopic mechanisms responsible for their very convenient properties.

One particular aspect that seems very promising both to gain fundamental knowledge and to produce even more efficient materials is the effect of atomic ordering on the properties of these alloys [2–5]. For instance, one may wonder whether some specific atomic arrangements can generate drastic and useful changes with respect to the usually grown disordered material. Examples of such changes are a large enhancement of the electromechanical responses of the system or moving its Curie temperature into a temperature range of interest. If such arrangements exist, identifying the microscopic origin of their unusual properties would definitely be of great fundamental and technological importance. Addressing these issues in an efficient manner requires (1) a computational technique able to accurately determine the properties of sufficiently large alloy configurations and providing at the same time a deep microscopic insight; and (2) the ability to find the right atomic ordering leading to a given prefixed property, i.e., to solve the so-called *inverse problem* [6].

The purpose of this Letter is to demonstrate that such an ideal situation is nowadays possible. More precisely, we have used the recently proposed first-principles derived effective-Hamiltonian method of Ref. [7] to tackle the inverse problem of designing and understanding ferroelectric alloys with prefixed properties. We focused on $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (PSN) alloy because Sc and Nb are chemically very different. (Note that Sc and Nb belong to different columns of the periodic table, which makes PSN a heterovalent alloy.) As a result, we expected that atomic ordering in PSN might lead to significant changes with respect to the disordered case. As a matter of fact, we found

that some arrangements between the Sc and Nb atoms (i) greatly enhance the electromechanical responses, (ii) lead to currently unobserved ground states of orthorhombic and monoclinic symmetries (while the disordered material adopts a well-known rhombohedral ground state), and (iii) can considerably shift the Curie temperature. Furthermore, the analysis of our findings suggests that the mechanism responsible for these anomalous features in PSN can be understood by simple electrostatic considerations and/or simple phenomenological models. Some promising directions for future experimental and theoretical research are also provided.

Modeling PSN.—We first describe the effective-Hamiltonian approach of PSN. One starts by using the so-called “virtual crystal approximation” [8] to create a simple system $\text{Pb}\langle\text{B}\rangle\text{O}_3$ in which $\langle\text{B}\rangle$ is a virtual atom involving a kind of average between Sc and Nb atoms. The relevant lattice distortions of $\text{Pb}\langle\text{B}\rangle\text{O}_3$ are described via a first-principles derived effective-Hamiltonian $H_{\text{eff}}^{\langle\text{B}\rangle}$ as the one used in Ref. [9] to simulate the finite-temperature properties of barium titanate. This Hamiltonian is then *corrected* to account for the presence of the two different B atoms in the real alloy. The complete Hamiltonian has the form

$$H_{\text{eff}}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\eta_l\}, \{\sigma_j\}) = H_{\text{eff}}^{\langle\text{B}\rangle}(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\eta_l\}) + \Delta E(\{\mathbf{u}_i\}, \{\mathbf{v}_i\}, \{\sigma_j\}), \quad (1)$$

where \mathbf{u}_i is the local soft mode in cell i , $\{\mathbf{v}_i\}$ are vectors related to the inhomogeneous strains, and $\{\eta_l\}$ are the homogeneous strains in Voigt notation. The *soft mode* \mathbf{u} is defined as the supercell average of the local modes: $\mathbf{u} = \frac{1}{N} \sum_i \mathbf{u}_i$, where N is the number of cells in the system [10]. The variables $\{\sigma_j\}$ characterize the atomic configuration: $\sigma_j = +1$ (respectively -1) indicates there is a Nb (respectively Sc) atom in cell j .

Essentially, the correction term for PSN has the form

$$\Delta E = \sum_i \sum_{j(i)} \sigma_j Q_{ji} \hat{\mathbf{e}}_{ji} \cdot \mathbf{u}_i, \quad (2)$$

where i runs over all the cells and j over the first three nearest-neighbor shells of cell i . Here, \mathbf{e}_{ji} is the unit vector joining the B site j to the B site i ; $\{Q_{ji}\}$ are the alloy-correction coefficients, which depend only on the distance between sites i and j . Interestingly, Eq. (2) can be rewritten as the interactions between the dipole moments $Z^*\mathbf{u}_i$ and radial fields \mathcal{E}_{ji} —the latter being generated by the σ_j , being dependent on $\{Q_{ji}\}$, and acting on the neighboring cells i —

$$\Delta E = -\sum_i Z^*\mathbf{u}_i \cdot \left[\sum_{j(i)} \mathcal{E}_{ji} \right] = -\sum_i Z^*\mathbf{u}_i \cdot \mathcal{E}_i, \quad (3)$$

where \mathcal{E}_i can be viewed as the total field acting on \mathbf{u}_i . We find that the first-principles calculated Q_{ji} parameters all have negative signs. As a result, the field \mathcal{E}_{ji} created on site i by a Sc (respectively Nb) atom sitting on a site j is *attractive* (respectively *repulsive*). This is consistent with an electrostatic picture of PSN resulting from the fact that Sc^{+3} (respectively Nb^{+5}) atoms are negatively (respectively positively) charged with respect to the average B -atom valence of $+4$; i.e., to some extent \mathcal{E}_{ji} can be viewed as the electric field created in site i by σ_j .

Equations (1)–(3) indicate that there is a competition in PSN between the global tendency of the system towards the ferroelectric ground state (GS) given by $H_{\text{eff}}^{(B)}$, which is of rhombohedral symmetry with the local modes all oriented along the same $\langle 111 \rangle$ direction [4], and the local tendency of the modes to align parallel to \mathcal{E}_i , which typically favors an inhomogeneous local-mode distribution and therefore a decrease of the magnitude of \mathbf{u} . Recent Monte Carlo simulations using this effective-Hamiltonian description of PSN have demonstrated its high accuracy to reproduce direct first-principles results in disordered, rocksalt-ordered (RS), and other nontrivially ordered structures [4,5]. These simulations also reproduce very well the finite-temperature experimental results for disordered PSN, once the simulation temperatures are linearly rescaled so that the calculated transition temperature coincides with the measured one [4,11]. On the other hand, accurately predicting the properties of samples with local compositions significantly different from the 50% average of Sc and Nb may require the use of higher-order correction terms in Eq. (2). Even so, we believe that all the *trends* discussed in this Letter are qualitatively correct since Eq. (2) includes the first-order (and thus the most important) correction terms.

Solving inverse problems.—The so-called *inverse Monte Carlo* is the most convenient computational scheme to search for the atomic ordering—i.e., the *solution sample*—leading to a prefixed property [6]. It is a Monte Carlo annealing done on the compositional variables σ_j , and controlled by an energy functional $\mathcal{O}[\{\sigma_j\}]$ that is defined so that its minimum—i.e., the result of the annealing procedure—corresponds to the solution sample we pursue. For instance, one would choose $\mathcal{O} = -|d_{34}|$ to determine the atomic configuration exhibiting the highest value of the d_{34} piezoelectric coefficient. Note

that we perform *direct* Monte Carlo simulations using the effective Hamiltonian of Eq. (1) to evaluate the energy functional $\mathcal{O}[\{\sigma_j\}]$ in every inverse Monte Carlo step. Such evaluations usually require a long computing time and, as a result, we typically restricted ourselves to the use of a $4 \times 4 \times 4$ supercell (320 atoms or 64 perovskite-like cells), which is smaller than the $12 \times 12 \times 12$ supercell of Refs. [5,7] but still much larger than those feasible by direct first-principles methods.

Tuning the GS structural properties of PSN.—We estimate the GS structural properties (denoted in the following by the “0” superscript) by computing the corresponding thermal-averaged values at 5 K. The inverse problems considered here are listed in Table I. We find that the RS sample maximizes the magnitude of the GS soft mode, which is consistent with the fact that the internal field \mathcal{E}_i is null in any cell i in this sample and, therefore, no inhomogeneous local-mode distribution resulting from Eq. (3) can exist. For all the other inverse problems indicated in Table I, the solution sample can be described by a single non-null $\sigma_{\mathbf{k}}$ coefficient defined as

$$\sigma_{\mathbf{k}} = \frac{1}{N} \sum_j \exp(i\mathbf{k} \cdot \mathbf{R}_j) \sigma_j, \quad (4)$$

where \mathbf{k} is a vector in the first Brillouin zone and \mathbf{R}_j is the lattice vector associated to cell j [12]. Our results show that the composition modulations described by $k_\alpha = 1/4 \equiv 3/4$ (which correspond to the “Nb-Nb-Sc-Sc” sequence along the α Cartesian direction) are related to the decrease of the α component u_α^0 of the GS soft mode. This result is a direct consequence of the electrostatic-related Eq. (3), since the other one-dimensional modulations compatible with the considered $4 \times 4 \times 4$ supercell—i.e., $k_\alpha = 0$ (“Nb-Nb-Nb-Nb” or “Sc-Sc-Sc-Sc”) and $k_\alpha = 1/2$ (“Nb-Sc-Nb-Sc”)—result in zero internal field along the α direction and therefore in no reduction of u_α^0 . Consequently, the sample defined by a single $\sigma_{\mathbf{k}}$ with $\mathbf{k} = (1/4, 1/4, 1/4)$ exhibits the rhombohedral GS with the smallest magnitude of the soft mode.

TABLE I. Inverse problems related to several GS properties of PSN. First column: energy functional \mathcal{O} . The “R” subscript indicates a rhombohedral symmetry [i.e., $\mathbf{u}_R = u_R(1, 1, 1)$]. Second column: solution configurations. “RS” stands for the rocksalt structure while we indicate the \mathbf{k} point leading to the non-null $\sigma_{\mathbf{k}}$ coefficient (see text) for the other cases. Third column: GS soft mode \mathbf{u}^0 . In one case, we indicate two “good” solutions. We include the information about the disordered sample for comparison.

\mathcal{O}	Sol. conf.	\mathbf{u}^0 (Bohr)
$- \mathbf{u}_R^0 ^2$	RS	(0.507, 0.507, 0.507)
$ \mathbf{u}_R^0 ^2$	(1/4, 1/4, 1/4)	(0.431, 0.431, 0.431)
$(u_z^0)^2$	(0, 0, 1/4)	(0.552, 0.552, 0.000)
	(1/2, 1/2, 1/4)	(0.484, 0.484, 0.000)
$(u_y^0)^2 + (u_z^0)^2$	(0, 1/4, 1/4)	(0.665, 0.242, 0.242)
	Disordered	(0.462, 0.461, 0.461)

Similarly, the modulations described by $\mathbf{k} = (0, 0, 1/4)$ and $\mathbf{k} = (1/2, 1/2, 1/4)$ present a “ $\Leftarrow \Rightarrow \Leftarrow$ ” sequence of very strong internal fields \mathcal{E}_i along the z direction. As a result, the z components of the local modes align parallel to these fields and the mean value u_z^0 is null. This indicates that PSN samples with an orthorhombic GS can be produced by conveniently arranging the Sc and Nb atoms. We also tried to produce a tetragonal GS but obtained only a partial success, namely a sample characterized by $\mathbf{k} = (0, 1/4, 1/4)$ with a monoclinic GS for which $|u_x^0| \gg |u_y^0| = |u_z^0|$. Interestingly, both orthorhombic and monoclinic phases have never been observed (yet) in PSN materials since the ground states of the two experimentally-grown samples (disordered and RS) are of rhombohedral symmetry [4].

Maximum electromechanical responses at low temperature.—We now consider the inverse problem of maximizing the electromechanical responses of PSN at 5 K [13]. We focus on the piezoelectric coefficient d_{34} and the dielectric susceptibility χ_{33} because we numerically find that they exhibit much larger values than any other coefficient. Interestingly, we also find that both of them reach their maximum values for the same atomic ordering. The solution sample exhibits $\chi_{33} = 8319$ and $d_{34} = 4868$ pC/N, to be compared with the values of 325 and 90 pC/N obtained in disordered PSN. A striking enhancement of the electromechanical response can thus be achieved by rearranging the Sc and Nb atoms. (We also obtained other samples with $\chi_{33} > 4000$ and $d_{34} > 2000$ pC/N, all sharing the structural features that we discuss in the following.) The GS of the solution sample is characterized by $\mathbf{u}^0 = (0.544, 0.567, 0.076)$, where the main feature is the small value of the z component of the soft mode. This reflects the fact that the $\sigma_{\mathbf{k}}$ coefficients that contribute most to the atomic ordering (around 70% of the total) have $k_z = 1/4$. Our results thus suggest that samples with a “+ + - -” composition modulation in the z direction, where “+” (respectively “-”) stands for a plane that is rich in Nb (respectively Sc), will simultaneously exhibit small values of u_z^0 and large values of χ_{33} and d_{34} at low temperatures. However, this modulation cannot be too strong since, for instance, we numerically found that the atomic configuration characterized by the single $\mathbf{k} = (0, 0, 1/4)$ (for which $u_z^0 = 0$, see Table I) has small electromechanical responses.

We now discuss the relationship between the small value of $|u_z^0|$ and the large electromechanical responses. Figure 1 shows the probability distribution of u_x and u_z corresponding to the Monte Carlo simulation at 5 K of the solution sample, as well as the free-energy map of the system around \mathbf{u}^0 . This latter is calculated out of the probability distribution as done in Ref. [14]. The two main features of Fig. 1 are (1) the *broadness* of the u_z distribution, which is responsible for the large value of χ_{33} (see Ref. [13]), and (2) the *flatness* of the corresponding free-energy well, which indicates the ease of rotating

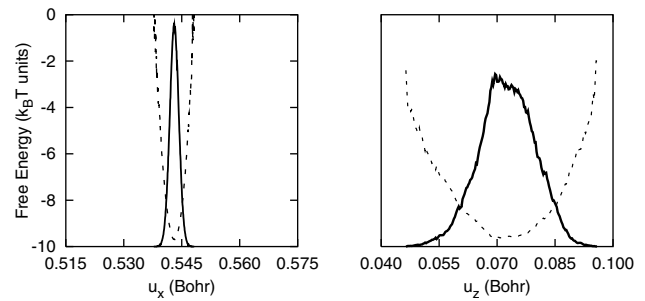


FIG. 1. Probability distribution of u_x and u_z at 5 K (solid line, in arbitrary units) and the corresponding free-energy map (dashed line, in $k_B T$ units indicated in the vertical axis) for the sample with the maximum responses discussed in the text. To obtain these results, we considered a $12 \times 12 \times 12$ supercell (trivially obtained from the $4 \times 4 \times 4$ solution sample by simple translation) and performed a 10^6 -sweep Monte Carlo simulation. Only the region around \mathbf{u}^0 is explored, and the results for u_y are essentially identical to those for u_x .

the polarization around u_z^0 . Interestingly, both features are typically associated with a small value of $|u_z^0|$ within the usual Devonshire-Landau description of ferroelectric perovskites [15]. Moreover, we numerically find that u_z and η_4 are strongly coupled in our effective Hamiltonian for PSN, which implies that their thermal fluctuations are very correlated. Consequently, according to Ref. [13], a large value of χ_{33} typically corresponds to a large value of d_{34} , as we indeed find.

Tuning the finite-temperature properties of PSN.—Studying PSN at finite (relatively high) temperatures requires long Monte Carlo simulations in order to obtain good statistics. Thus, due to computational limitations we decided not to *directly* solve finite-temperature (FT) inverse problems. However, some links between the GS and FT properties are expected on the basis of well-known models that share some essential features with our effective-Hamiltonian description of PSN. More precisely, the so-called ϕ^4 model [16] suggests the following relationship: the larger the value of $|u^0|$, the deeper the corresponding free-energy well at 0 K and, therefore, the higher the Curie temperature T_c . Hence, we thought it was pertinent to check whether the Curie temperature of PSN could be tuned by changing the value of the GS soft mode. Consequently, we studied the FT behavior of four samples that all undergo a single cubic to rhombohedral transition but exhibit different values for their GS soft modes. Our results, shown in Fig. 2, confirm that it is indeed possible to move the Curie temperature to a temperature range of interest by designing alloys with a prefixed value of $|u^0|$. It is remarkable that relatively small changes in the GS soft mode result in such large variations in T_c . Interestingly, the transition of the sample with the smallest $|u^0|$ takes place near room temperature. It is important to notice that one can tune the FT electromechanical responses of the system by moving T_c , because these responses reach their

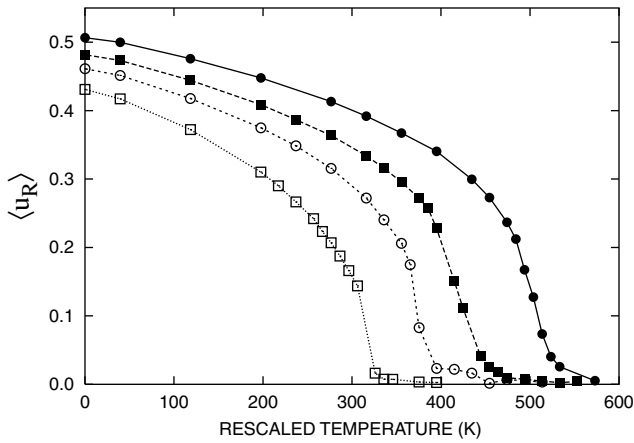


FIG. 2. Temperature evolution of $\langle u_R \rangle$ (see caption of Table I) for four PSN samples. These samples all undergo a single (cubic to rhombohedral) phase transition, and are chosen so as to exhibit different values of the GS soft mode. The values of u_R^0 considered here are 0.507 Bohr (RS, which exhibits the largest possible value of u_R^0), 0.484 Bohr (an intermediate sample generated by solving the appropriate inverse problem), 0.461 Bohr (disordered sample), and 0.431 Bohr (the sample defined by $\mathbf{k} = (1/4, 1/4, 1/4)$, which exhibits the lowest possible value of u_R^0). All the results correspond to the 2×10^5 -sweep Monte Carlo simulation of a $12 \times 12 \times 12$ supercell, which thus guarantees a good convergence in the calculated transition temperatures. The temperatures have been rescaled so that the calculated T_c of the disordered sample (944 K) coincides with the experimental value (373 K).

maximum values around the paraelectric to ferroelectric transition.

In summary, we have implemented a method to solve inverse problems in perovskite alloys by using the first-principles effective-Hamiltonian approach of Ref. [7], and applied it to PSN. We predict that the system properties (GS symmetry, electromechanical responses, Curie temperature, etc.) can be greatly modified by varying the atomic ordering. Furthermore, all the anomalous features we predict can be essentially understood by simple electrostatic considerations and/or simple phenomenological models. As a result, (1) we have indicated which kinds of alloy structures may lead to currently unobserved structural phases as well as to giant dielectric and piezoelectric responses, and (2) we expect similar results to occur in other heterovalent perovskite alloys. Finally, we hope that our predictions will stimulate attempts at experimental growth of such samples.

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- [1] See, for example, K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer Academic Publishers, Boston, 1996); S.-E. Park and T.R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997); O. Auciello, J.F. Scott, and R. Ramamoorthy, *Phys. Today* **51**, No. 7, 22 (1998).
- [2] M.A. Akbas and A.M. Davies, *J. Am. Ceram. Soc.* **81**, 670 (1998).
- [3] N. Sai, B. Meyer, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5636 (2000).
- [4] R. Hemphill, L. Bellaiche, A. García, and D. Vanderbilt, *Appl. Phys. Lett.* **77**, 3642 (2000).
- [5] A.M. George and L. Bellaiche, *Phys. Rev. B* **64**, 060102 (2001).
- [6] See A. Franceschetti and A. Zunger, *Nature (London)* **402**, 60 (1999); W. Scheweika, *Disordered Alloys* (Springer-Verlag, Berlin, 1998) for a more general discussion.
- [7] L. Bellaiche, A. García, and D. Vanderbilt, *Phys. Rev. Lett.* **84**, 5427 (2000).
- [8] L. Bellaiche and D. Vanderbilt, *Phys. Rev. B* **61**, 7877 (2000).
- [9] W. Zhong, D. Vanderbilt, and K.M. Rabe, *Phys. Rev. Lett.* **73**, 1861 (1994); *Phys. Rev. B* **52**, 6301 (1995).
- [10] Note that the polarization of the simulated system is given by $(Z^*/v)\mathbf{u}$, where Z^* is the Born effective charge associated to the local soft modes and v is the unit cell volume.
- [11] This linear rescaling has previously yielded a very good agreement between simulation and experiment for BaTiO₃ [see Alberto García and David Vanderbilt, in *Proceedings of the First-Principles Calculations for Ferroelectrics: Fifth Williamsburg Workshop*, edited by R.E. Cohen, AIP Conf. Proc. No. 436 (AIP, New York, 1998), p. 53], and Pb(Zr_{1-x}Ti_x)O₃ [7].
- [12] We omit the $2\pi/a$ factors of the wave vectors, where a is the lattice parameter of the perovskite-like cell.
- [13] The response coefficients are expressed in the orthonormal basis formed by $\mathbf{a}_1 = [100]$, $\mathbf{a}_2 = [010]$, and $\mathbf{a}_3 = [001]$, and are calculated as done by A. García and D. Vanderbilt, *Appl. Phys. Lett.* **72**, 2981 (1998). Essentially, we have $\chi_{33} \propto (\langle u_z^2 \rangle - \langle u_z \rangle^2)$ and $d_{34} \propto (\langle u_z \eta_4 \rangle - \langle u_z \rangle \langle \eta_4 \rangle)$, where the thermal averages correspond to a simulation with neither electric field nor stress applied.
- [14] S. Radescu, I. Etxebarria, and J.M. Pérez-Mato, *J. Phys. Condens. Matter* **7**, 585 (1995).
- [15] A.F. Devonshire, *Phyl. Mag.* **40**, 1040 (1949). See also J. Íñiguez, S. Ivantchev, J.M. Pérez-Mato, and A. García, *Phys. Rev. B* **63**, 144 103 (2001), and references therein.
- [16] A.D. Bruce, *Adv. Phys.* **29**, 111 (1980). Note that the effective Hamiltonians based on the approach developed in Ref. [9] can be viewed as a generalized ϕ^4 model in which three-dimensional local modes and long-range interactions are considered.