Determination of ferroelectric compositional phase transition using novel virtual crystal approach

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Abstract. We employ a new method for studying compositionally disordered ferroelectric oxides. This method is based on the virtual crystal approximation (VCA), in which two or more component potentials are averaged into a composite atomic potential. In our method, we construct a virtual atom with the correctly averaged atomic size and atomic eigenvalues. We have used our new method to study the composition dependent phase transition in Pb(Zr$_{1-x}$Ti$_x$)O$_3$ lying between $x = 0.5$ and $x = 0.4$. We correctly predict the experimentally determined phase transition from the tetragonal phase to a low-temperature rhombohedral phase between these two compositions.

INTRODUCTION

Our recent work [1] has demonstrated the utility of the virtual crystal approximation (VCA) [2,3] to study compositionally disordered materials. Following our initial VCA study of a stress-induced phase transition in Pb(Zr$_{1-x}$Ti$_x$)O$_3$, we and other authors have extended the VCA to studies of compositional phase transitions [4], temperature-dependent phase transitions [5], and dynamical properties. [6] Prior to this the VCA has had some success in providing qualitative, and in some instances quantitative agreement with large-scale solid-state calculations.

Previous implementations of the VCA have focused on the averaging of two or more component potentials in separable form at the solid-state level. [7,8] By averaging the potentials, it is difficult to assess the quality of the resulting VCA potential. In some studies, these traditional VCA potentials have yielded unphysical results. [9,10] Speculation has been made in the literature that it is the inability of these traditional VCA potentials to capture the important differences in chemical bonding and ionicity accurately that has given the poor results. [9]
METHODOLOGY

Due to the inconsistencies in the literature regarding the quality of VCA results, we have recently formulated a new approach for the construction of VCA potentials. Our method represents a simple and intuitive way to construct VCA potentials and assess their quality. It is a severe departure from the more traditional methods for VCA potential construction. We have previously presented a thorough description of our method for the construction of VCA atoms. [1,4] For brevity, we will only present here the salient points of our method.

• Our method averages the component atoms at the all-electron level, such that all-electron eigenvalues, potentials, wave functions and charge density are all computed for the virtual atom. Since the solution of the all-electron atom is common to all pseudopotential procedures, our method is general enough to be used in all types of pseudopotential construction.

Operationally we find the all-electron wave functions and eigenvalues for the atoms we want to average. We then determine the properly averaged eigenvalues for the VCA atom valence states from the eigenvalues of the all-electron atoms. We then construct a bare Coulombic potential from the properly averaged bare nuclear potentials of the component atoms and a properly averaged core charge density. In doing so, we have insured that the resulting VCA potential will have the correct averaged size. Using this averaged nuclear potential and frozen-core charge density, we construct new self-consistent wave functions for the VCA atom valence states. We require that these new wave functions solve the Kohn-Sham equations in the valence region and give the properly averaged eigenvalues.

• From this new set of potentials and wave functions, we construct an optimized pseudopotential. [11] This method enforces the exact agreement of the VCA eigenvalues with the averaged all-electron eigenvalues for the reference state only. For any other electronic configuration, we have made no requirements on the quality of the potential. Recently, we have formulated the designed nonlocal pseudopotential method, [12] in which we exploit the inherent arbitrary separation of the local potential and semilocal correction terms required for the Kleinman-Bylander separable form. [13] By adjusting the form of the local potential and therefore the correction terms, we may dramatically improve the transferability of the potential without affecting the exact agreement at the reference configuration. This transferability improvement over a wide range of electronic configurations insures correct ionicity and polarizability of the virtual atom.

It is our assertion that the preservation of the proper averaged size of the VCA potential and a high level of transferability will provide accurate VCA atoms which yield excellent agreement with superlattice calculations. We have previously demonstrated the effectiveness of our new VCA approach. [1,4] The remainder of this paper will focus on the construction and use of two VCA potentials to study the compositional phase transition in Pb(Zr_{1-x}Ti_{x})O_x.
RESULTS AND DISCUSSION

We have applied our new VCA method to the Zr\textsubscript{1−x}Ti\textsubscript{x} virtual atom for \(x = 0.5\) and \(x = 0.4\). All atomic energy calculations were done with the local density approximation and optimized [11] and designed nonlocal pseudopotential [12] methods were employed. The generation parameters for the two VCA potentials are included in Table 1. For all atoms, semi-core states were included as valence. It is important to note that although we have included multiple \(s\)-channel states, only one \(s\) nonlocal projector is used. For both VCA atoms, we have used the \(s\)-potential with the addition of one or two square-step potentials as the local potential.

The transferability testing results for the two VCA potentials are contained in Table 2. From the table, it is evident that our new VCA pseudopotentials are highly transferable at either value of \(x\).

We use both VCA potentials in solid-state calculations for three structural phases of Pb(Zr\textsubscript{1−x}Ti\textsubscript{x})O\textsubscript{3}. The electronic wave functions are expanded in a plane-wave basis using a cutoff energy of 50 Ry. We included the 5\(d\) shell as valence for the Pb atom as well as including scalar relativistic effects. Brillouin zone integrations are approximated accurately as sums on a 4\(\times\)4\(\times\)4 Monkhorst-Pack \(k\)-point mesh. [14]

We have included three structurally distinct phases of Pb(Zr\textsubscript{1−x}Ti\textsubscript{x})O\textsubscript{3} in the current studies of compositions between \(x = 0.5\) and \(x = 0.4\): a tetragonal Ti-rich \(P4mm\) and two rhombohedral Zr-rich (\(R3c\) and \(R3m\)) phases. [15,16] Around 400-500K, the rhombohedral region exhibits a boundary between \(R3c\) (low-temperature) and \(R3m\) (high-temperature) phases, which depends weakly on composition. [17,18] The \(R3c\) phase shows complex oxygen octahedral tilting, which doubles the primitive unit cell to ten atoms. [19]

We have completed full electronic and structural relaxations for five-atom unit cells for the tetragonal and high-temperature rhombohedral phases. Due to the complex oxygen octahedral distortions, we have used a 10-atom unit cell for the low-temperature rhombohedral phase.

| TABLE 1. Construction parameters for the Zr\textsubscript{1−x}Ti\textsubscript{x} virtual crystal (VCA) designed nonlocal pseudopotentials. The VCA potentials were generated with the methods described in references [11], [12] and the method described in text. Core radii (\(r_c\)) are in atomic units, \(q_c\) parameters are in \(\text{Ry}^{1/2}\), step widths are in atomic units and step heights are in \(\text{Ry}\). |
|---|---|---|---|
| Atom | \(r_c\) | \(q_c\) | Step Range | Step Height |
| VCA (\(s^2p^6d^0\)) | 1.38, 1.51, 1.40 | 7.07 | 0.00–0.56 | 1.18 |
| \(x = 0.5\) | | | 0.56–0.79 | 1.34 |
| VCA (\(s^2p^6d^0\)) | 1.27, 1.38, 1.61 | 7.07 | 0.00–1.25 | 10.32 |
| \(x = 0.4\) | | | | |
TABLE 2. Configuration testing for Zr$_{1-x}$Ti$_x$ virtual crystal (VCA) atoms generated with the method described in text. Averaged eigenvalues and total energy differences are given for Zr and Ti pseudopotentials (PS) for two values of $x$. The PS construction parameters have been presented elsewhere. [1,4] Errors are computed as a difference between VCA and averaged PS results. All energies are in Ry.

| State | $x = 0.5$ | | $x = 0.4$ | |
|-------|----------------|----------------|----------------|----------------|
|       | PS | VCA | Error | PS | VCA | Error |
| $s^2$ | -7.5701 | 0.0000 | -7.4266 | 0.0000 |
| $p^6$ | -5.9530 | 0.0000 | -5.8303 | 0.0000 |
| $s^0$ | -2.5581 | -0.0038 | -2.5280 | -0.0029 |
| $d^0$ | -3.4488 | 0.0000 | -3.3629 | 0.0000 |
| $\Delta E_{tot}$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| $s^2$ | -6.7808 | 0.0016 | -6.6490 | 0.0019 |
| $p^6$ | -5.1720 | 0.0015 | -5.0611 | 0.0017 |
| $s^1$ | -2.0304 | -0.0009 | -2.0061 | -0.0013 |
| $d^0$ | -2.7034 | 0.0041 | -2.6316 | 0.0050 |
| $\Delta E_{tot}$ | -2.3067 | -0.0019 | -2.2790 | -0.0014 |
| $s^2$ | -6.3652 | -0.0031 | -6.2570 | -0.0027 |
| $p^6$ | -4.7744 | -0.0049 | -4.6868 | -0.0038 |
| $s^0$ | -1.8399 | 0.0000 | -1.8234 | 0.0004 |
| $d^1$ | -2.3571 | -0.0033 | -2.3087 | -0.0047 |
| $\Delta E_{tot}$ | -2.8936 | -0.0012 | -2.8270 | -0.0007 |
| $s^2$ | -5.6586 | -0.0029 | -5.5599 | -0.0023 |
| $p^6$ | -4.0734 | -0.0047 | -3.9953 | -0.0040 |
| $s^1$ | -1.3453 | 0.0011 | -1.3327 | 0.0019 |
| $d^1$ | -1.6889 | -0.0018 | -1.6517 | -0.0010 |
| $\Delta E_{tot}$ | -4.4923 | -0.0004 | -4.4107 | 0.0005 |
| $s^2$ | -4.1730 | -0.0077 | -4.1060 | -0.0061 |
| $p^6$ | -2.6064 | -0.0106 | -2.5597 | -0.0091 |
| $s^2$ | -0.3293 | 0.0018 | -0.3285 | 0.0026 |
| $d^2$ | -0.3239 | -0.0072 | -0.3193 | -0.0058 |
| $\Delta E_{tot}$ | -6.2696 | -0.0037 | -6.1628 | -0.0022 |

bohedral phase. For all rhombohedral calculations, we have neglected the small shear relaxations.

In Figure 1, we show the equations of state for the three phases of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ at
$x = 0.5$. We find the tetragonal phase is the ground-state structure for this composition lying approximately 0.05 eV lower in energy than both rhombohedral phases. This is correct energy ordering found experimentally. [15,16]

![Figure 1](image1.png)

**FIGURE 1.** Equations of state for the tetragonal (solid line), high-temperature rhombohedral (dotted-dashed line) phase and low-temperature rhombohedral (dotted line) phases of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ for $x = 0.5$. The heights and energies are for a 40-atom unit cell.

In Figure 2, we show the equations of state for the three phases of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ at $x = 0.4$. We find both rhombohedral phases have shifted down in energy relative to the tetragonal phase. In fact, the low-temperature rhombohedral phase has shifted by approximately 0.09 eV in energy and therefore becomes the ground-state structure for this composition of Pb(Zr$_{1-x}$Ti$_x$)O$_3$. This result is in direct agreement with the experimental findings [15,16] and demonstrates the ability of our new VCA method to locate and predict compositional phase transitions.

**CONCLUSIONS**

In this paper, we have applied our new method for constructing a virtual crystal pseudopotential to the Zr and Ti atoms. Potentials constructed with our method not only possess the properly averaged atomic size but also a high level of accuracy in describing energetic differences due to changes in both ionicity and polarizability. This method is based on averaging all-electron information and therefore makes the method applicable to all types of pseudopotential construction algorithms. We have used our new method
FIGURE 2. Equations of state for the tetragonal (solid line), high-temperature rhombohedral (dotted-dashed line) phase and low-temperature rhombohedral (dotted line) phases of Pb(Zr$_{1-x}$Ti$_x$)O$_3$ for $x = 0.4$. The heights and energies are for a 40-atom unit cell.

to construct two Zr$_{1-x}$Ti$_x$ VCA potentials at $x = 0.5$ and $x = 0.4$. With these potentials, we have studied three structural phase of Pb(Zr$_{1-x}$Ti$_x$)O$_3$, finding that the tetragonal phase is the ground-state structure for Pb(Zr$_{1-x}$Ti$_x$)O$_3$ at $x = 0.5$. When moving to $x = 0.4$, we find that the low-temperature rhombohedral phase becomes the ground-state. This finding is in excellent agreement with experiment and represents the first ab initio determination of a compositionally-dependent phase transition in a ferroelectric oxide.

Recently yet another phase (monoclinic $Cm$) has been experimentally found at low temperatures for compositions between $x = 0.45$ and $x = 0.5$. [20] We plan to extend the current research by studying the monoclinic phases with our VCA atoms.

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