Silver solid solution piezoelectrics

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Using density functional theory calculations, we investigate the feasibility of using silver on the perovskite A-site in high-performance lead-free piezoelectrics. The calculations show that silver atoms are ferroelectrically active and can off-center by 0.5 Å. To induce Ag ferroelectric behavior absent in pure AgNbO3 we explore solid solutions of AgNbO3 with well-known simple perovskites PbTiO3, BaZrO3, and BaTiO3. For the AgNbO3–PbTiO3 solid solution, we predict a morphotropic phase boundary near (AgNbO3)0.38(PbTiO3)0.62. We find an unusual sequence of compositional phase transitions in AgNbO3–BaZrO3 and AgNbO3–BaTiO3 which are due to the effects of volume expansion in perovskites. For the AgNbO3–BaTiO3 solid solution we find two morphotropic phase boundaries at 12.5% and 37.5% AgNbO3 compositions with favorable piezoelectric properties and indications of high Tc.

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Piezoelectric lead-based perovskite solid solutions are used in many important technological applications, such as medical imaging devices and Navy SONAR. The search for new materials with better piezoelectric performance, higher curie ferroelectric to paraelectric transition temperatures Tc, and lower toxicity is currently an area of active experimental and theoretical research. Off-centering of the Pb atoms on the perovskite A-site has been shown to be crucial to the high performance of the current materials, such as PbZr1-x,TiO3 (PZT), with the large 0.5 Å Pb distortions giving rise to large internal polarization P and strong coupling to electric fields.

In this study, we examine the use of silver-based perovskites in piezo-electrics. While pure AgNbO3 is either weak ferroelectric or antiferroelectric, alloying with other perovskites may give rise to strong ferroelectricity and good piezoelectric properties.

We use density functional theory (DFT) calculations with the local density approximation for the exchange-correlation functional for all calculations. Forty atom 2×2×2 supercells with Cartesian lattice vectors and periodic boundary conditions were used to represent the solid solutions studied. We choose a cation arrangement that maximizes the distances between cations of the same charge for each composition, leading to a rocksalt ordering on both A and B sites for the 50/50 composition. In the real material the cation arrangement will most likely be disordered; however, we find that the variations in cation orderings studied for some of compositions change the results presented here only slightly. In ionic relaxations, no symmetry was imposed, and lattice constants were optimized at the experimental (for end-member compounds) or interpolated (for solid solutions) experimental volume. The lack of imposed symmetry allows use to find low-symmetry monoclinic phase directly by our DFT calculations. The Brillouin zone was sampled using a 2×2×2 Monkhorst-Pack k-point mesh. We used designed nonlocal12,13 optimized pseudopotentials14 to represent the core correlations in the calculations. P was computed using atomic Born effective charges Z* obtained with the Berry phase approach15 in parent simple perovskites. This approach was recently used to successfully model piezoelectric behavior of PZT.17 We also compared P values obtained from Z* with direct Berry phase calculations for some solid solution compositions, and the results were in agreement. To check if the structures obtained by our calculations are chemically reasonable, we used bond-valence analysis,18 which showed only small deviations from ideal ionic valences for all relaxed structures.

We look for materials which exhibit improvement over the current PZT or BaTiO3 (BT) piezoelectrics in three desired properties: piezoelectric performance, Tc, and lower toxicity. In order to determine if the proposed materials are likely to be good piezoelectrics, we examine P values and the energy difference between rhombohedral (R) and tetragonal (T) phases (ΔE(R-T)). Materials with large P will couple strongly to an applied electric field; a small (ΔE(R-T)) indicates the presence of a monoclinic (M) phase at the morphotropic phase boundary (MPB) crucial for easy polarization rotation and high piezoelectric performance. High Tc is favored by a large energy difference between the distorted polarized structure and the nonpolar high symmetry structure (ferroelectric instability ΔE(PF), and high Tc is disfavored by large octahedral rotations. Elimination of Pb atoms from the A-site makes a material environmentally friendly.

We first investigate pure AgNbO3 (AN), an experimentally well-studied perovskite, using 5-atom and 40-atom unit cells. In agreement with experimental data on low temperature phase of AN, our relaxed 40-atom structures exhibit mixed ferroelectric and antiferroelectric character and large 14.5° octahedral rotations typical for perovskites with low tolerance factor t (t=0.95 for AN),

\[ t = \frac{R_{A-O}}{R_{B-O}} \],

(1)

where RA-O is the sum of A and O ionic radii and RB-O is the sum of B and O ionic radii. We find that short covalent Ag–O bonds are a requirement of the Ag–O bonding on the A-site, similar to the short covalent bonds found in many Pb-based perovskites. In our 40-atom AN calculations, the short Ag–O bonds are created through octahedral rotations,
TABLE I. Results of DFT calculations for compositions of ANPT, ANBZ, and ANBT solid solutions closest to MPB. MPB locations are estimated based on linear interpolations shown in Fig. 1. Results for BT and 50/50 PZT are given for comparison. MPB content is in percent, $P$ magnitudes are in $C/m^2$, $\Delta E_{FE}$ values are in $meV$ per 5-atom cell, average $O_6$ rotation angles are in degrees. The values for 50/50 PZT are taken from Refs. 18, 21, and 27.

<table>
<thead>
<tr>
<th>% AN at MPB</th>
<th>$P$</th>
<th>$\Delta E_{FE}$</th>
<th>$O_6$ rot angle</th>
<th>Lead free</th>
<th>$\epsilon_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>...</td>
<td>0.24</td>
<td>16</td>
<td>0.0</td>
<td>Y</td>
</tr>
<tr>
<td>PZT</td>
<td>...</td>
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<td>117</td>
<td>2.0</td>
<td>N</td>
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<tr>
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<td>0.60</td>
<td>45</td>
<td>7.7</td>
<td>N</td>
</tr>
<tr>
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<td>24</td>
<td>5.9</td>
<td>Y</td>
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<td>0.32</td>
<td>48</td>
<td>0.4</td>
<td>Y</td>
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<td>0.44</td>
<td>26</td>
<td>5.0</td>
<td>Y</td>
</tr>
</tbody>
</table>

FIG. 1. Energy difference between rhombohedral and tetragonal phases as a function of AgNbO$_3$ content for ANPT (solid), ANBZ (dashed), and ANBT (dotted) solid solutions. Positive $\Delta E_{FE}$ values indicate that tetragonal phase is preferred. For ANBZ the preferred phase at 50% AN content is actually orthorhombic.

with small 0.1 Å Ag displacements. In the small 5-atom unit cell, octahedral rotations are not possible by symmetry, and the short Ag–O bonds are created through 0.5 Å off-center displacements. In both supercells, Nb atoms move off center by 0.22 Å. For the 5-atom AgNbO$_3$, we compute a $P$ of 0.67 $C/m^2$, somewhat smaller than 0.85 $C/m^2$ calculated for PbTiO$_3$ (PT) but more than twice as large as 0.24 $C/m^2$ calculated for BaTiO$_3$(BT). At the same time we find that the 2 $meV/5$-atom cell energy cost of $P$ rotation from (100) to (111) direction is the same as that in BT and much smaller than 33 $meV/5$-atom cell in PT. This indicates that if $O_6$ rotations were eliminated, AgNbO$_3$ would be a good piezoelectric material.

We now examine three ways to unlock ferroelectricity and Ag off-centering in AgNbO$_3$ by studying three solid solutions. First, we alloy AN with PT. The strong preference of PT for displacive instability would decrease $O_6$ rotations and induce large Ag cation distortions. This is similar to the ferroelectricity induced in PbZrO$_3$ by addition of a small amount of PT. Due to the presence of Pb atoms, this solid solution will still be toxic. Nevertheless, it may exhibit improvement in other desired properties. Second, we alloy AN with BaZrO$_3$ (BZ), a perovskite of much larger volume. Recent theoretical calculations have shown that large perovskite volume expansion under “negative pressure” leads to an anomalous increase in tetragonality and very large cation displacements. Alloving AN with BZ is a way of realizing such negative pressure experimentally. Third, since perovskites with tolerance factor greater than one are usually ferroelectric, we alloy AN ($t=0.95$) with BT ($t=0.106$) to increase $t$ and induce ferroelectricity. This strategy can also be thought of as a combination of the first two approaches, as BT exhibits both ferroelectric distortions and a higher volume than AN. For all three solid solutions, we focus on compositions from 0 to 50% AN content. (Higher AN concentrations lead to structures with large $O_6$ rotations and low magnitude of $P$.) The results for $\Delta E_{R-T}$ are presented in Fig. 1 and $P$ magnitudes, $\Delta E_{FE}$ values, and average $O_6$ rotation angles at MPB of each solution are presented in Table I.

We find that while the ANPT system should exhibit good piezoelectric performance, the $T_C$ most likely will not be higher than that of current PZT materials. Our calculations predict a standard phase diagram with a $T\rightarrow M\rightarrow R$ sequence of phase transitions with decreasing PT content and a $M_A$ phase with polarization in the (100) plane around 37.5% AN composition. At this composition, the small energy differences between the T, M and R phases as found by DFT ($<1$ $meV/5$-atom cell)) together with the large 0.6 $C/m^2$ $P$ at MPB indicated good piezoelectric performance. However, $T_C$ at MPB will most likely be significantly reduced from the PT $T_C$ due to a decrease in $\Delta E_{FE}$ and large $O_6$ rotations (7.7° versus 2.0° in 50/50 (PZT)$^{27}$). Finally, the presence of the Pb atoms on the A-site makes this proposed material environmentally unfriendly and difficult to synthesize in a pure bulk form due to formation of the competing pyrochlore phase commonly found in perovskites with both Pb and Nb. $^{29}$

The ANBZ solid solution is not likely to exhibit either a high $T_C$ or improved piezoelectric performance. Around the MPB composition (37.5% AN), the $P$ is comparable to that of BT and $t$ oriented in the (110) plane corresponding to the $M_C$ phase between a tetragonal and orthorhombic (O) phases. While the $\Delta E_{FE}$ is enhanced compared to BT, the octahedral rotations are large. These results suggest that ANBZ will most likely be only a small improvement on BT. However, this solid solution displays an interesting $C\rightarrow T\rightarrow M\rightarrow O$ sequence of compositional phase transitions and a nonmonotonic dependence of $\Delta E_{R-T}$ on AN content which can be understood by considering the implication of previous work on anomalous tetragonality. $^{25}$

In a solid solution, alloying a perovskite of a small volume into a perovskite of large volume expands the A site for the smaller A cation. This can be though of as applying negative pressure to the smaller perovskite. Tetragonality of the solid solution is favored both by a larger negative pressure, (i.e., a larger average system volume), and by a greater fraction of the smaller A-cation sites under negative pressure. Since these two effects have opposite dependence on AN concentration, $\Delta E_{R-T}$ can be expected to exhibit the nonmonotonic dependence on AN content, as is observed in our DFT calculation.

The ANBZ phase diagram is reminiscent of the phase diagram of the PbZrO$_3$–BaZrO$_3$ solid solution, $^{10}$ where alloying the antiferroelectric (AFE) PbZrO$_3$ into the large volume BZ produces a C (PE) $\rightarrow R$ (FE) $\rightarrow O$ (AFE) sequence of compositional phase transition. Similar phase diagrams should be seen in other systems where ferroelectric behavior is induced in a nonferroelectric material by volume expansion.
Our results for the ANBT system indicate that it is a promising candidate for high performance lead-free piezoelectrics. This system has a rich phase diagram with R → M_A → T → M_A → R phase transition sequence due to the volume expansion effects as explained earlier for the ANBZ solid solution. The two MPBs are located around 12.5% and 50% AN content, with \( P \) values enhanced relative to BT and comparable to the \( P \) of some of the current single crystal lead based materials.\(^3\)

For both MPB compositions, \( \Delta E_{FE} \) values are significantly increased relative to BT, with small \( O_6 \) rotations for the 12.5% AN composition; for 50% AN composition the 5° rotations are larger than 2° rotations found in 50/50 PZT.\(^28\) For these two promising compositions, we also computed the \( e_{33} \) piezoelectric coefficients. The computed \( e_{33} \) values were 9.5 and 14.5 C/m\(^2\) for the 12.5% AN and 50% AN compositions, respectively. These values are comparable to the \( 12.6 \) C/m\(^2\) computed and 11.6 C/m\(^2\) measured for 50/50 PZT solid solution.\(^17\) While the 50% AN composition has superior piezoelectric properties, due to the larger internal \( P \) and smaller computed energy differences between the T, M_A, and R phases, the 12.5% AN compositions should have a higher \( T_C \).

In summary, we have shown that Ag cations can be ferroelectrically active on the perovskite A-site. Alloying AgNbO\(_3\) with PbTiO\(_3\) leads to a standard phase diagram with MPB around 37.5% AgNbO\(_3\) composition. Alloying AgNbO\(_3\) into paraelectric BaZrO\(_3\) induces ferroelectricity and leads to an unusual phase transition sequence which can be explained by the recently studied negative pressure volume expansion effects. A similar phase diagram is obtained for the AgNbO\(_3\)–BaTiO\(_3\) solution, which also displays good piezoelectric properties at the two MPB locations. The ANBT solid solutions should also display a higher \( T_C \) than BaTiO\(_3\). The interesting properties exhibited by silver solid solutions make them promising candidates for experimental investigation.

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15. Z* are 1.4, 2.7, 3.66, 6.3, and 9.5 for Ag, Ba, Pb, Zr, Ti, and Nb cations, respectively. These values are in close agreement with experimental results. Oxygens Z* vary depending on the direction and cation neighbors, with net dynamic charge \( \Sigma Z_{ij}^* \approx 0 \).
25. P. K. Davies (private communication).
27. We actually find the T phase to be preferred at 12.5% AN content (see Fig. 1) but the heuristic rule that a monoclinic phase is associated with a small \( \Delta E_{FE} \) suggests that a MPB and a MA phase are present between 0 and 12.5% AN concentration.