

high Born charge.<sup>16</sup> Furthermore, experimental work on the BiScO<sub>3</sub> - PT solid solution shows an MPB with enhanced Curie temperature,<sup>17</sup> and there have been recent studies of several other Bi-based perovskites in solid solutions with PT.<sup>18–22</sup> One problem has been that while the small Bi-ion tends to enhance tetragonality on the tetragonal side of the MPB, this same effect may prevent the occurrence of an MPB, leading to phase diagrams with only tetragonal phases.

Recently, an extremely large tetragonality ( $c/a \sim 1.11$  and high Curie temperature  $T_C$  of  $\sim 700$  °C at  $x = 0.6$  was reported for perovskite solution  $(1 - x)\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3 - (x)\text{PbTiO}_3$ .<sup>23</sup> This is reminiscent of the behavior of CdTiO<sub>3</sub> - PT alloys, which also have highly enhanced tetragonality.<sup>24–26</sup> In perovskites the balance between tetragonal and rhombohedral states is generally controlled by a balance between the energy lowering due to tetragonal strain, which favors the tetragonal state, and the  $B$ -site off-centering, which favors a rhombohedral state<sup>27</sup> (note that with small  $A$ -site ions there is an additional stabilization of the tetragonal state because off-centerings along  $[001]$  directions are towards the most open face of the O cage around the  $A$ -site; therefore, this direction is favored for the  $A$ -site and this can be important if the displacement is very large<sup>8</sup>). The interplay of  $A$ -site and  $B$ -site off-centering, and the importance of the  $B$ -site in determining the direction of the ferroelectric polarization suggests the exploration of alternate  $B$ -site ions in solid solutions with PT to obtain an MPBs.

Here, we present a study of the polar behavior of perovskite  $(\text{Bi,Pb})(\text{Zn,Nb})\text{O}_6$  and  $(\text{Bi,Sr})(\text{Zn,Nb})\text{O}_6$  using density functional supercell calculations. The purpose is to explore the effect of combining the mechanisms discussed above in a perovskite that may be amenable to experimental synthesis. Specifically, the compositions explored have different size  $A$ -site cations (Pb and Bi), stereochemically active ions on the  $A$ -site (particularly, Bi, though Pb may also contribute as discussed below), and ions with electronic structures that favor cross-gap hybridization and therefore ferroelectricity on the  $B$ -site (Nb and Zn).

As mentioned, one motivation for this study is to explore the use of different size  $A$ -site ions in relation to stereochemical activity to obtain  $A$ -site driven ferroelectricity. The ionic radii<sup>2</sup> of the  $A$ -site ions considered here are  $r_{\text{Pb}^{2+}} = 1.63$  Å,  $r_{\text{Sr}^{2+}} = 1.58$  Å, and  $r_{\text{Bi}^{3+}} = 1.31$  Å. Thus, Bi<sup>3+</sup> is significantly smaller than the other  $A$ -site ions and Pb and Sr have approximately the same size, but unlike Sr, Pb has stereochemical activity that can favor ferroelectricity, as in PbTiO<sub>3</sub>.

Related to this there is an experimental report of the synthesis and some physical properties of perovskite  $(\text{Bi}_{0.5}\text{Sr}_{0.5})(\text{Mg}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ,  $(\text{Bi}_{0.5}\text{Ba}_{0.5})(\text{Mg}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ,  $(\text{Bi}_{0.5}\text{Sr}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ,  $(\text{Bi}_{0.5}\text{Ba}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{0.5})\text{O}_3$ , and the solid solution of  $(\text{Bi}_{0.5}\text{Ba}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{0.5})\text{O}_3$  with PT and  $(\text{Bi}_{0.5}\text{Sr}_{0.5})(\text{Mg}_{0.5}\text{Nb}_{0.5})\text{O}_3$  with SrTiO<sub>3</sub>.<sup>28,29</sup> The compound  $(\text{Bi}_{0.5}\text{Sr}_{0.5})(\text{Mg}_{0.5}\text{Nb}_{0.5})\text{O}_3$  was reported to be

ferroelectric based on the observation of a hysteresis loop below 103 K. All four compounds were reported to show phase transitions above room temperature and relatively high dielectric constants. They also show substantial microwave loss, which may indicate ferroelectricity.

## II. APPROACH

The perovskite alloys were studied using supercell calculations within density functional theory. The main results are for compositions BiPbNbZnO<sub>6</sub> and BiSrNbZnO<sub>6</sub>. The large charge difference between Zn<sup>2+</sup> and Nb<sup>5+</sup> may be expected to lead to a strong ordering tendency on the  $B$ -site. This is the case in the relaxor systems PbZn<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> (PZN) and PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> (PMN), where a double perovskite like structure occurs even though the Nb:Zn stoichiometry is not 1:1 (specifically, in PZN and PMN one double perovskite  $B$ -site sublattice is Nb and the other is 1/3 Nb and 2/3 Zn or Mg, which in turn may further order).<sup>30–32</sup> In the present case the stoichiometry is 1:1, which should further stabilize the ordering. Therefore we assume an ordering of the  $B$ -site lattice into a double perovskite structure. In contrast, there is no a priori reason to assume that the  $A$ -site lattice consisting of Pb and Bi is chemically ordered.

BiPbZnNbO<sub>6</sub> (BPZN) and BiSrZnNbO<sub>6</sub> (BSZN) have ferroelectrically active ions on both the  $A$  and  $B$  sites. On the  $B$ -site both Zn<sup>2+</sup> and Nb<sup>5+</sup> favor ferroelectricity, as is evident from the stronger relaxor ferroelectricity of PZN relative to PMN and the ferroelectricity of KNbO<sub>3</sub>. Likewise Bi<sup>3+</sup> and Pb<sup>2+</sup> are stereochemically active, and favor ferroelectricity on the perovskite  $A$ -site. However, both BPZN and BSZN are expected to be strongly  $A$ -site driven materials both based on ionic radius ( $t < 1$ , and  $A$ -site size disorder) and lone pair physics,<sup>27</sup> and as such a competition between octahedral tilts and polar off-centering may be expected similar to the Pb(Zr,Ti)O<sub>3</sub> system.<sup>33</sup> Therefore it is important that the supercells are constructed in a way that this competition can be included. The minimum size for this is 2x2x2, or 40 atoms, since such a cell has an even number of units along the  $[001]$ ,  $[011]$ , and  $[111]$  directions and therefore can accommodate the various Glazer tilt patterns.<sup>34</sup>

An additional constraint comes from the fact that with multiple  $A$ -site ions it is possible to choose cells that have polar spacegroups just because of the cation ordering and not because of lattice instability. This would not represent ferroelectricity, but would rather simply be an artifact of the selected order. Therefore even though Bi and Pb are not expected to chemically order in the solid solutions, we consider them in a highly ordered state within our supercells. Here we select a rock-salt ordering of Pb and Bi on the  $A$ -site. The cation ordering with this choice has symmetry  $F\bar{4}3m$ , which is non-polar. Thus any polarization or off-centering is a consequence of lattice instability and not the choice of cation ordering, and furthermore, one may expect that a more disordered alloy