

FIG. 3: (color online) Electronic DOS of the pseudocubic relaxed BiPbZnNbO₆ supercell on a per formula unit basis. The top panel shows the total DOS and the Bi *s* and Pb *s* projections. The bottom panel shows Bi *p*, Pb *p*, Nb *d*, Zn *sp* and O *p* projections. The projections are the integrals of components of the charge density with given angular character within the LAPW spheres. Note that for extended orbitals this gives an underestimate. The energy zero is set at the valence band maximum.

and PbTiO₃.^{27,38} These displacements would yield a point charge polarization based on nominal charges of 58 $\mu\text{C}/\text{cm}^2$ using nominal charges, with the largest contributions coming from the Bi and Nb (note the +5 charge state of Nb). The actual polarization is higher (see below) because the nominal charges are enhanced due to covalency.

As is usual in perovskite ferroelectrics, we find that the ferroelectricity is enhanced as the volume is expanded and conversely under compression. However, over the volume range investigated (pseudocubic lattice parameter, 3.88 Å $\leq a \leq$ 4.07 Å), the material remains ferroelectric, with cation displacements along [111]. The average cation displacements as a function of *a* are given in Table I. The LDA typically underestimates lattice parameters, often by $\sim 1\text{--}2\%$, and as such the prediction of ferroelectricity in this material would seem to be robust

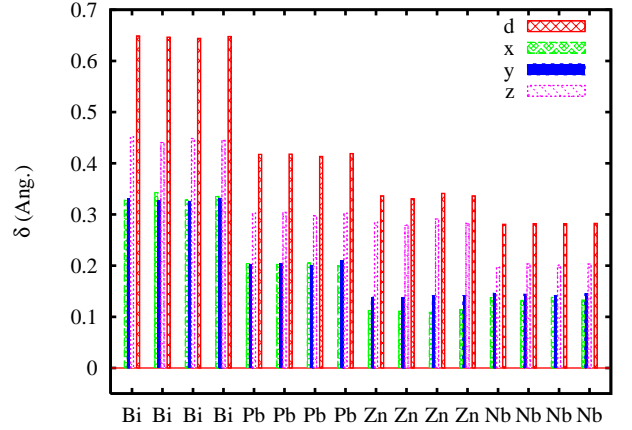


FIG. 4: (color online) Cation off-centerings along the Cartesian directions with respect to their O cages for the various sites in LDA relaxed structure of the 40 atom supercell of BiPbZnNbO₆ at the same volume as in Fig. 2, but with an imposed *c/a* ratio of 1.0606. Note that despite the large tetragonal strain the cation displacements remain nearly collinear and do remain reasonably close to a [111] direction.

TABLE I: Average displacements of the cations relative to their O cages in relaxed 40 atom BiPbZnNbO₆ cells as a function of pseudocubic lattice parameter, *a*.

<i>a</i> (Å)	δ_{Bi} (Å)	δ_{Pb} (Å)	δ_{Zn} (Å)	δ_{Nb} (Å)
3.88	0.50	0.28	0.20	0.22
3.92	0.54	0.31	0.23	0.24
3.98	0.62	0.38	0.26	0.27
3.99	0.64	0.39	0.27	0.27
4.03	0.69	0.44	0.30	0.30
4.07	0.75	0.50	0.35	0.32

against LDA volume errors.

We now discuss the electronic structure as it relates to ferroelectricity. The electronic density of states (DOS) and projections for the relaxed supercell are shown in Fig. 3. The calculated LDA band gap is 2.7 eV. This is almost certainly an underestimate due to the LDA band gap error. Considering the sizable gap and the fact that all the ions are in chemically stable valence states it is likely that BiPbZnNbO₆ can be made as a good insulator at ambient temperature. This is an important consideration for a ferroelectric material to be used in applications. The stereochemical activity of Bi³⁺ and Pb²⁺ is associated with the lone pair chemistry, which is usually discussed in terms of a high polarizability of the electrons in the occupied 6*s* orbitals of these ions. As shown, the Bi 6*s* states give rise to the DOS peak centered at -9.5 eV relative to the valence band maximum (VBM), while the Pb 6*s* states are at -7.4 eV. The O 2*p* bands provide the DOS from -6 eV to the VBM, while the conduction bands are derived from unoccupied orbitals of metal character, primarily Nb 4*d*, Bi 6*p*, Pb 6*p* and at higher energies, Zn *sp* character. There is a modest hybridization between the Bi and Pb 6*s* states and the O