Ab Initio Study of the Effect of Uniaxial Pressure on the Ferroelectric Properties of PbTiO$_3$

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Abstract. We have studied the effect of uniaxial pressure on the ferroelectric properties of PbTiO$_3$ by using a first principles electronic structure method. The pressure is applied in the $ab$-plane. The magnitude of the ferroelectric lattice distortion is found to increase as the pressure is increased. Short Ti-O bonds along the $c$-direction are found to remain almost constant in length whereas the stretched Ti-O bonds become more stretched because of an increase in the equilibrium lattice constant in the $c$-direction. The thermodynamic stability of the ferroelectric phase over the paraelectric phase increases as pressure is applied.

INTRODUCTION

Ferroelectric (FE) materials have been extensively studied in recent years because of their promising properties for nonvolatile random access memories as well as several other applications [1]. In a typical FDRAM setup a ferroelectric material is grown on an electrode (or vice versa). In most cases there is a relatively large lattice mismatch at the interface. Usually the electrode material has a smaller lattice constant in the plane of the interface. For thin films, which are most interesting from a technological point of view, this effectively causes a compressive uniaxial pressure on the FE-film. Despite of its obvious technological importance the effect of uniaxial pressure on FE thin films is not widely studied using the $ab$ – $initio$ electronic structure methods. Ramer et. al. have studied the effect of uniaxial pressure on 50/50 PZT, they found that pressure induces a tetragonal-to-rhombohedral phase transition [3].

We have studied the effect of compressive uniaxial pressure on PbTiO$_3$ by using a first principles electronic structure method [2]. We chose to work on lead titanate (PbTiO$_3$) since it has a simple phase diagram. We are restricted to perform simulations at zero temperature, but for PbTiO$_3$ this is not a problem, since the zero
temperature phase is the tetragonal ferroelectric phase. The displacive ferroelectric lattice distortion and the $c/a$ ratio in PbTiO$_3$ are the largest among simple perovskite FEs.

Our plane-wave pseudopotential calculations are based on the density functional theory (DFT) within local density approximation [6]. *Ab initio* simulations have been successfully applied to ferroelectric materials to explain the microscopic mechanism of the spontaneous polarization [7,8] and phase diagrams [5,9]. In our earlier papers similar methods have been used to study defects [10–12] and domain walls [13] in PbTiO$_3$. In our calculations norm-conserving nonlocal [14] Vanderbilt type ultrasoft pseudopotentials [15] for Pb, Ti, and O are used. The energy cutoff $E_{\text{cut}}$ for the plane-wave expansion was 35 Ry. Brillouin zone (BZ) sampling was done using a $4 \times 4 \times 4$ Monkhorst-Pack mesh [17]. The calculated lattice constant for the ferroelectric tetragonal phase is 3.85 Å, which is about 1.4% smaller than the experimental one [16]. The calculated equilibrium $c/a$ value is 1.055, which is slightly smaller than experimental value of 1.063. These numbers are well in line with previously published studies [18,19].

## RESULTS

The change in the total energy of PbTiO$_3$ as the lattice constant in the $ab$-plane is varied is shown in the Figure 1 a) for ferro-, paraelectric tetragonal, as well as for the cubic phases. For the ferroelectric phase both the atomic coordinates and the $c/a$ ratio are optimized for each value of the $ab$-plane lattice constant. As the lattice constant in the $ab$-plane is reduced, the lattice constant along the $c$-axis increases (see Fig. 2 b)) leading to a relatively small changes in the volume

![Figure 1](image-url)
FIGURE 2. a) Ti-O bond lengths along the c-axis as a function of lattice constant in the ab-plane. Short bond lengths remain almost constant as the ab-lattice shrinks. b) The c/a-ratio as a function of lattice constant in ab-plane. All distances are given in Å’s.

II CONCLUSIONS

Our results show that the ferroelectric phase becomes more stable with respect to the paraelectric phase as compressive pressure is applied in the ab-plane. Also the polarization of the unit cell increases as pressure is applied. Since the polarization is along c-axis, an increase in c/a-ratio reduces the probability of other than up/down domain. Our results indicate that the ferroelectric properties of thin films grown on a substrate, with a smaller lattice constant than the FE material should be better than ones grown on lattice matched substrates. It is, however, seen experimentally that depositing electrode material to a FE thin film in small droplets leads to better results than as depositing as one large area (total area of the electrode...
is the same in both cases). The compressive pressure applied to a film is larger when the electrode is deposited in one large patch and should therefore behave better according to our result. This difference between our result and experimental findings indicates that there must be lattice imperfections which dominate the behavior change as the strain in the $ab$-plane is increased. It could be that the formation of defects becomes more favorable as uniaxial pressure is applied and therefore the performance is reduced even though for a perfect lattice the trend should be the opposite.

REFERENCES

1. See, for example, J. F. Scott, Ferroelectrics Review 1, 1 (1998).