

# Pb-driven anti-ferroelectric phase in $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ : First-principle study

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## Abstract

Density functional calculations are used to investigate the role of Pb displacement in the formation of anti-ferroelectric phase in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . Order and disordered supercells, both are used. Through geometry optimization without symmetry imposed, the two supercells are found to be anti-ferroelectric. Displacement of cations are analyzed and it is shown that asymmetry of Pb's next-nearest B-site shell is probably the reason for anti-parallel displacement of Pb. A–B-site, B-site–O bond distances and  $\text{O}_6$  octahedral volumes are also calculated.  
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Perovskite structure  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) is of great interest, both as a prototypical Pb-containing relaxor ferroelectric [1] and as an end member of the technologically important [2,3]  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $\text{PbTiO}_3$  (PMN–PT) solid solution. PMN is a relaxor having a large, broad and frequency-dependent peak in the dielectric constant versus temperature [2] at around 300 K, and it has the  $\text{ABO}_3$  type perovskite structure with  $\text{Nb}^{5+}$  and  $\text{Mg}^{2+}$  cations presenting in a stoichiometric ratio to keep the charge balanced. As a Pb-containing perovskite, ferroelectricity in PMN is driven primarily by the stereochemical activity of Pb, the B-site ions play an important role both in the production of the morphotropic boundaries and facile polarization rotation that underlies the piezoelectric performance [4].

Recently several first-principle studies of the structural and dynamical behavior of PMN have been performed [5–10]. Choudhury et al. [6,7] studied different phase in PMN and calculated Born effective charges whose highly anisotropic contributed to huge electromechanical coupling. In their work, anti-ferroelectric (AFE) phase was predicted. Anti-ferroelectric

fluctuations were also investigated using synchrotron X-ray scattering, and competition between randomly occurring anti-ferroelectric and ferroelectric fluctuations may be responsible for the relaxor behavior in PMN [11–13]. However, the microscopic origin of the AFE phase is not fully understood. From a microscopic point of view, lattice instabilities of perovskite material can often be understood in terms of tolerance factor [14], and both Pb–O and B-site–O hybridization are also important [15]. In previous first-principle work it has been proposed that in Pb-containing perovskite solid solutions such as  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  [10] and PMN–PT [16], Pb displacements are the driven force for the phase transition. So we performed first-principle calculations to throw some lights on the role of Pb in the formation of AFE phase in PMN.

Because 1:1 B-site order in polar nanoregions was widely admitted [11,17], two kinds of supercell models for PMN were usually used in DFT calculations. One model is a 30-atoms supercell based on a 1:1 ordering along [111] direction, consisting of a NaCl ordering of two sublattice, the first of Nb and the second of composition  $\text{Mg}_{2/3}\text{Nb}_{1/3}$  with layering of Mg and Nb in (111) planes on mixed sublattice. Another model is a 15-atom supercell based on 1:2 ordering constructed by tripling the simple cubic perovskite cell along the [001] direction. After geometry optimization, the former model is of

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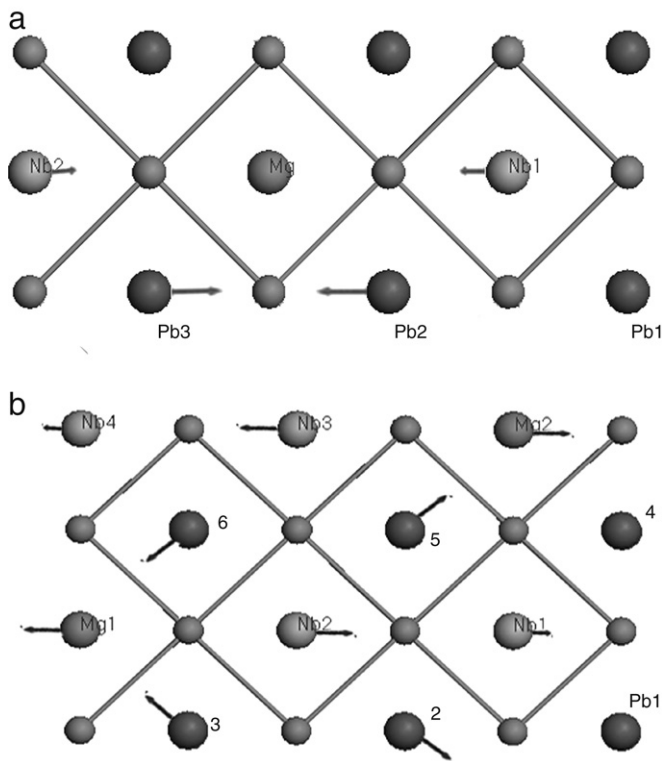


Fig. 1. Relaxed structures of supercell I (a) and II (b). They are both projections of supercells at experimental lattice constant on  $y$ - $z$  plane. Arrows show the displacement of atoms from perfect perovskite positions. Pb atoms are 1/2 unit cell above the plane, and apical O atoms are omitted.

ferroelectric (FE) with a polarization along (111) [9], while the latter model is of AFE [6,9]. As we focus on the AFE phase in PMN in this work, we choose the latter model in our calculations. However, there maybe disorder regions in real PMN. By taking into account this point, we also use a 30-atom supercell in our calculations. This supercell can be thought of as snapshots of small regions of the real disordered solution. It has one-unit-cell periodicity in the  $x$ -direction. Such periodicity is of course absent in real material. But as proved in previous *ab initio* study, this  $x$ -direction short periodicity does not affect the accuracy of the results [18]. Since DFT calculations using local density approximation (LDA) tend to underestimate lattice constant and also ferroelectricity is sensitivity dependent on the volume of the material, we used the experimental lattice constant for all the calculations, which is 4.049 Å for a cubic perovskite primitive cell [19]. It has shown that lattice instabilities are generally reliable when the lattice parameters have their experimental values [20]. The supercells we used are shown in Fig. 1.

The DFT calculations were done using the planewave-pseudopotential method. Perdew–Zunger [21] local density approximation (LDA) was used for the exchange–correlation functional. We use ultra-soft pseudopotentials [22] for Pb, O and Nb, and Bachelet–Hamann–Schlueter [23] norm-conserving pseudopotentials for Mg, as implemented in the ESPRESSO code [24]. The Pb (5d, 6s and 6p), Mg (3s and 3p), Nb (4s, 4p, 4d and 5s), O (2s and 2p) were treated as valence. A plane wave basis with kinetic energy cutoff of 30 Ry is used to

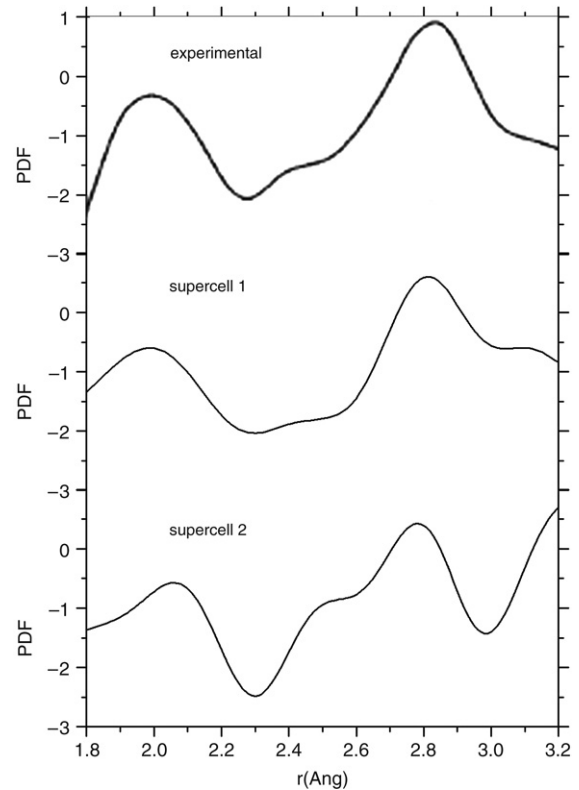


Fig. 2. Comparison of PDFs obtained from the relaxed structures of two supercells and from the experimental results (Ref. [23]).

ensure the convergence in all the calculations presented here. During the geometry optimization, the convergence criterion is satisfied when all components of all forces are smaller than  $10^{-3}$  a.u. All calculations on the  $1 \times 1 \times 3$  15-atom supercells were done with a  $4 \times 4 \times 2$  Monkhorst–Park  $k$ -point sampling of Brillouin zone. For  $1 \times 2 \times 3$  30-atom supercells, we used a  $4 \times 2 \times 2$  Monkhorst–Park grid.

Geometry optimization is achieved from ideal perovskite structures, by only allowing the internal atomic positions to relax, while no symmetry is imposed. The pair distribution functions (PDFs) obtained from our relaxed structure for PMN are shown in Fig. 2. The PDF provides information about the interatomic distance in PMN. The first peak at about 2.0 Å is due to the B-site–O nearest neighbors, and the second peak at about 2.8 Å is due to Pb–O and O–O pairs. The PDF of supercell I fits better with the experimental one than that of supercell II, because compositional long-range order occurs in real PMN [25] and supercell I is ordered, while supercell II is disordered. As can be seen that our results are in good agreement with neutron-scattering experiments [26], this indicates that our supercells are sufficient for capturing the local structure of PMN.

The relaxed structures are shown in Fig. 1. Displacement directions of cations are shown by arrows. The two relaxed supercells both are AFE, with anti-parallel polarization along [001]. Our results are in good agreement with previous work [6, 8,9]. One can see that in supercell I, due to the symmetry along  $z$ -direction, two Nb atoms are equivalent, and Pb2, Pb3 does as well. In supercell II, Pb1 and Pb4, Pb2 and Pb5, Pb3 and Pb6,

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