



# First-principles Predictions of Structures and Piezoelectric Properties of $\text{PbTiO}_3$ Single Crystal

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Using the various exchange-correlation functionals, such as LDA, GGA-PBE, GGA-PBESol and GGA-AM05 functionals, first principle studies were conducted to determine the structures of paraelectric and ferroelectric  $\text{PbTiO}_3$ . Based on the structures determined by the various functionals, the piezoelectric properties of  $\text{PbTiO}_3$  are predicted under the density-functional perturbation theory (DFPT). The present prediction with the various GGA functionals are closer to the experimental findings compared to the LDA values. The present DFT calculations using the GGA-PBESol functional estimate the experimental data more reasonably than the conventional LDA and GGA functionals. The GGA-AM05 functional also predicts the experimental data as well as the GGA-PBESol. The piezoelectric tensor calculated with PBESol is relatively insensitive to pressure.

**Keywords:** First principle calculation, Piezoelectricity, Lead titanate

## 1. INTRODUCTION

Piezoelectric materials have a very important role in modern industries and are widely used as key materials in transducers, resonators, filters, and sensors. Discovered in 1880 by Pierre and Jacques Curie, piezoelectricity is a phenomenon whereby material becomes electrically polarized upon the application of stress. Complex insulating perovskite alloys are currently of great interest for use based on the exceptional piezoelectric properties. Examples include the  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) solid solutions that are currently used in piezoelectric transducers and actuators, and

most recently, the class of  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $\text{PbTiO}_3$  (PMN-PT) and  $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $\text{PbTiO}_3$  (PZN-PT) materials which, when synthesized in single-crystal form, exhibit remarkably large piezoelectric constants and maximum strain levels. These materials promise dramatic improvements in the resolution and range of ultrasonic and SONAR listening devices. Moreover, new piezoelectric materials with excellent piezoelectric response combined with high temperature operation capabilities are currently sought. A fundamental understanding of factors that influence the piezoelectric properties of materials are of high scientific and technological value, but remains difficult to forecast.

Since the 1970s, scientists have persisted with efforts to make theoretic effort forecasting feasible. Due to rapidly increasing calculation speed and memory capacity of supercomputer and establish of modern polarization theory, direct quantitative calculation of piezoelectric coefficient of some relatively simple piezoelectric systems and qualitative forecasting of piezoelectric coefficient of some ferroelectric system from first principles

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are now possible. Based on the Kohn-Sham formulation [1], the density-functional theory (DFT) [2] has been used to calculate large systems where *ab-initio* Hartree-Fock calculation is not possible. Also, the density-functional perturbation theory (DFPT) [3] has been shown to give successful descriptions of the dielectric and piezoelectric properties of a wide range of materials in which electronic correlations are not too strong. The use of DFPT methods is becoming increasingly popular because of the ability to directly compute response properties.

Most previous DFT studies have employed the local density approximation (LDA) and the generalized gradient approximation (GGA) functionals to explain the exchange-correlation energy. The gradient corrected Perdew-Burke-Ernzerhof (PBE) [4] functional has been regarded as the standard GGA. For the lattice constant of solids, which is one of the most important factors in predicting mechanical and piezoelectric properties, LDA clearly underestimates the lattice constants whereas the GGA-PBE overestimates lattice constants to a similar degree. This discrepancy between the experiments and the predictions is intensified for the solids having d- and f-valence electrons, such as transition metals and their oxides. Recently, to improve the lattice constants of solids, new GGA functionals (PBE for solids, PBEsol [5] and AM05 [6]) have been suggested, and were shown to improve over PBE for various solids including transition metals.

In the present work, under the DFT, we investigate the physical properties of  $\text{PbTiO}_3$  (PT), which is one of the simplest ferroelectric oxide. Furthermore, because PT has a high Curie temperature,  $T_c = 766$  K, it is considered one of the most important end-component of the promising single crystal piezoelectric perovskites, such as PZT, PMN-PT, PZN-PT, and PMN-PIN( $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ )-PT. By employing LDA, GGA-PBE, GGA-PBEsol, GGA-AM05, we calculate static dielectric matrix, stiffness matrix and ion-clamped piezoelectric tensor at zero temperature. By comparing the DFT predictions with the available experimental results, we suggest more reliable functionals for the further studies, i.e. for the predictions of physical properties of PMN-PT, PZN-PT, and PMN-PIN-PT, which are being actively studied for the real applications.

## 2. METHODOLOGY

In the present spin-polarized DFT calculations, the well-established Vienna *ab initio* simulation package (VASP) [7,8] was used. We used augmented projected augmented wave (PAW) pseudopotentials, and included the  $5d^{10}$  and  $3s^23p^6$  electrons as the valence electrons for Pb and Ti, i.e., Pb  $5d$ ,  $6s$ ,  $6p$ , Ti,  $3s$ ,  $3p$ ,  $3d$ ,  $4s$ , and O  $2s$  and  $2p$  orbital-electrons were treated as valence electrons. The exchange-correlation energy was considered by employing the various functionals such as, LDA, GGA-PBE, GGA-PBEsol and GGA-AM05. A plane-wave cutoff energy of 700eV was used for static structure energy simulations and piezoelectric properties calculations. The Brillouin zone integration was performed using a  $6 \times 6 \times 6$  Monkhorst-Pack k-point mesh, by testing the convergence with respect to k-point mesh number. All atoms were relaxed using the conjugate gradient method until residual forces on constituent atoms became smaller than  $5 \times 10^{-2}$  eV/Å. The convergence of atomic configurations and relative energies were carefully checked with respect to plane-wave energy cutoff.

## 3. RESULTS AND DISCUSSION

Energy-volume behaviors of the ferroelectric and paraelectric phases of  $\text{PbTiO}_3$  are shown in Fig. 1, where the PBEsol functional is used. Energetics of the system supports that lowest sym-

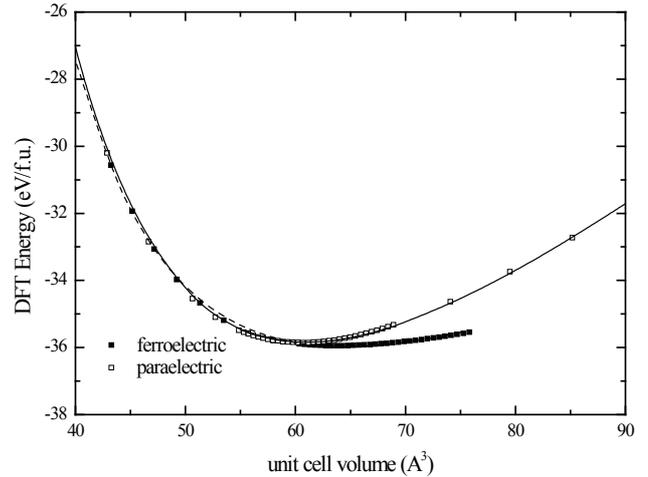


Fig. 1. The FE and the PE phases energies per the formula unit (f.u) of  $\text{PbTiO}_3$  with respect to unit cell volume ( $\text{Å}^3$ ). GGA-PBEsol functional is used. Lines are Murnaghan fit results which will be discussed later.

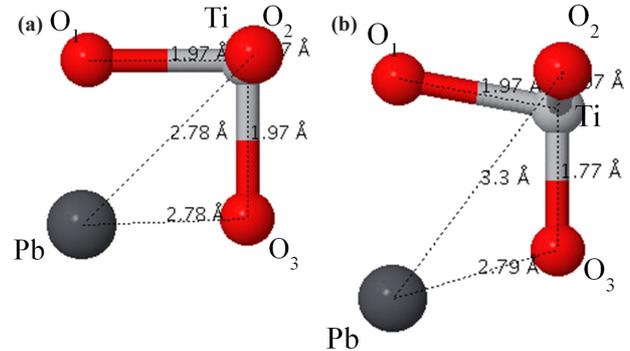


Fig. 2. Optimized structures of (a) the paraelectric cubic phase and (b) the ferroelectric tetragonal phase of  $\text{PbTiO}_3$ . GGA-PBEsol functional is used.

Table 1. Structural parameter of cubic paraelectric  $\text{PbTiO}_3$

	LDA	GGA-PBE	GGA-PBEsol	GGA-AM05	Exp.a	Exp.b
$a$	3.89	3.97	3.93	3.94	3.97	3.97

<sup>a</sup>data at the Curie temperature (766K) given in Mabud and Glazer [9].

<sup>b</sup>data at the Curie temperature (766K) given in Jona and Shirane [10].

metry structure is the structure with the lowest energy. We can determine the minimum energy and the corresponding most stable structures given in Figs. 2(a) and 2(b). The cubic structure of  $\text{PbTiO}_3$  is completely described by the lattice constant  $a$ . The calculated structures of paraelectric cubic  $\text{PbTiO}_3$  using the various functionals are compared with the existing experimental data in Table 1. In comparison between the theoretical results with the experimental data, the temperature effect between the experimental data which are obtained at the Curie temperature ( $T_c = 766$  K) and the present calculation which corresponds to zero temperature should be considered. Because the ions in paraelectric (PE) phase keep their symmetric cubic positions, the bond lengths of Ti-O and Pb-O are  $a/2$  and  $\sqrt{2}a$ , respectively.

The tetragonal structure of  $\text{PbTiO}_3$  is completely described by the lattice constant  $a$ , the ratio  $c/a$ , and by the displacement of ion

**Table 2.** Structural parameters and bond lengths of tetragonal ferroelectric PbTiO<sub>3</sub>. The displacement of ion their symmetric positions along the vertical z-direction ( $\delta z$ ) are given in terms of the lattice constant  $c$ .

	LDA	GGA-PBE	GGA-PBEsol	GGA-AM05	Expa	Expb
$a$	3.8566	3.9102	3.886	3.873	3.902	3.904
$c/a$	1.044	1.1254	1.094	1.110	1.065	1.063
$\delta z_{\text{Pb}}$	0.000	0.000	0.000	0.000	0.000	0.000
$\delta z_{\text{Ti}}$	0.0276	0.0478	0.0416	0.0444	0.038	0.040
$\delta z_{\text{O}_{1,02}}$	0.1000	0.1419	0.1238	0.1354	0.112	0.112
$\delta z_{\text{O}_3}$	0.0775	0.1480	0.1169	0.1353	0.117	0.112
Ti-O <sub>1,2</sub>	1.95	2.00	1.97	1.98		1.98
Ti-O <sub>3</sub>	1.81	1.76	1.77	1.76		1.78
Pb-O <sub>1,2</sub>	3.09	3.44	3.3	3.35		3.20
Pb-O <sub>3</sub>	2.74	2.84	2.79	2.80		2.80

<sup>a</sup>room temperature data of Mabud and Glazer [9].

<sup>b</sup>room temperature data given in Jona and Shirane [10].

their symmetric positions along the vertical z-direction ( $\delta z$ ). The present calculation results using different functionals are summarized in Table 2, where all structural parameters determined by fully unconstrained calculations are compared with experimental data at room temperature. As expected, the traditional LDA functional underestimates the lattice parameter and bond lengths, whereas the GGA-PBE overestimates. However, the recently suggested GGA-PBEsol gives a result that is comparable or is in better agreement with the experimental data. Considering the temperature effect shown in Mabud and Galzer [9], the agreement between the present with GGA-PBEsol and experiment is much improved. These configurations are used in further mechanical and piezoelectric properties calculations. The GGA-AM05 functional also predicts the experimental data as well as the GGA-PBEsol.

Generally, at constant temperature, the bulk modulus is defined by:

$$K = -V \left( \frac{\partial P}{\partial V} \right)_T \quad (1)$$

Murnaghan [11] assumed that the bulk modulus is a linear function of pressure as

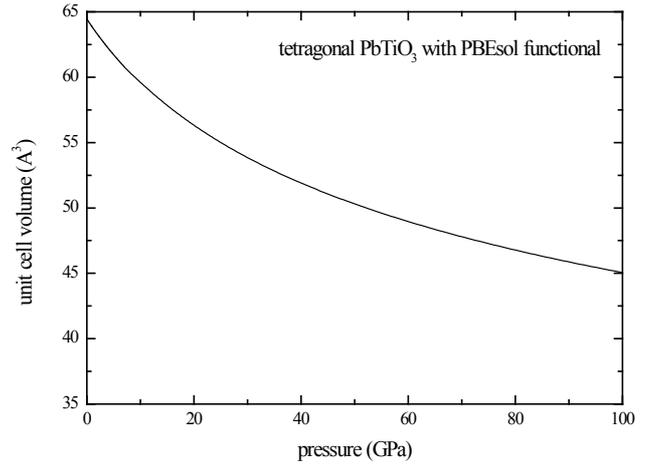
$$K = K_0 + K_0' P \quad (2)$$

By integrating Eq. (1) with Eq. (2), we can get the following Murnaghan equation:

$$P(V) = \frac{K_0}{K_0'} \left[ \left( \frac{V}{V_0} \right)^{-K_0'} - 1 \right] \quad (3)$$

Also, we can also express the volume depending on the pressure:

$$V(P) = V_0 \left[ 1 + P \left( \frac{K_0'}{K_0} \right) \right]^{-1/K_0'} \quad (4)$$



**Fig. 3.** Pressure-volume relation of the tetragonal ferroelectric PbTiO<sub>3</sub>.

Because in the present study we obtained the energy as a function of the volume, the following equation which connect the energy with volume is more useful:

$$E(V) = E_0 + K_0 V_0 \left[ \frac{1}{K_0' (K_0' - 1)} \left( \frac{V}{V_0} \right)^{-1-K_0'} + \frac{1}{K_0' V_0} - \frac{1}{K_0' - 1} \right] \quad (5)$$

The above equation is obtained by integrating Eq. (3) according to the relationship  $P = -(\partial E / \partial V)_T$ . The regression results with Eq. (5) are already given in Fig. 1. For the ferroelectric tetragonal phase of PbTiO<sub>3</sub>, the bulk modulus at the fully relaxed state is  $K_0 = 104 \text{ GPa}$  which is comparable with the previous experimental results [12-14]. Based on the calculation data given in Fig. 1, volume-pressure relation for the ferroelectric tetragonal phase of PbTiO<sub>3</sub> is summarized in Fig. 3.

Using the fully-relaxed structures, the piezoelectric tensor is determined by the density-functional perturbation theory (DFPT). In the present study, we calculated the piezoelectric tensor  $e_{ij}$  which connects the induced polarization  $P_i$  and strain tensor element  $\epsilon_j$  as

$$P_i = \sum_j e_{ij} \epsilon_j \quad (6)$$

The tetragonal phase PbTiO<sub>3</sub> is polarized along the (001) axis. For a tetragonal lattice the three piezoelectric constants  $e_{3,1}(=e_{3,2})$ ,  $e_{3,3}$  and  $e_{1,5}(=e_{2,4})$  are sufficient to describe the piezoelectric effects. Additionally,  $e_{3,1}(=e_{3,2})$  and  $e_{3,3}$  describe the zero field polarization induced along the z-axis when crystal is uniformly strained in the basal xy-plane or along the z-axis, respectively. Yet,  $e_{1,5}(=e_{2,4})$  represents the change of polarization perpendicular to the z-axis induced by shear strain. In a tetragonal crystal, the induced polarizations are related as

$$P_1 = e_{15} \epsilon_2, P_2 = e_{15} \epsilon_4 \text{ and } P_3 = e_{33} \epsilon_3 + e_{31} (\epsilon_1 + \epsilon_2). \quad (7a, b \& c)$$

**Table 3.** Piezoelectric stress tensor elements ( $C/m^2$ ) of ferroelectric tetragonal  $PbTiO_3$ .

	$e_{15}$	$e_{31}$	$e_{33}$
LDA	6.73	1.68	6.14
GGA-PBE	3.68	1.49	3.94
GGA-PBEsol	3.14	1.42	4.48
GGA-AM05	2.86	1.40	4.15
Exp. [12]	3.29	-0.98	3.35
Exp. [14]	2.96	0.46	6.50
Exp. [13]	4.4	2.1	5.0
Exp. [13]	4.8	-0.67	4.1

**Table 4.** Predicted piezoelectric stress tensor elements ( $C/m^2$ ) of ferroelectric tetragonal  $PbTiO_3$ . PBEsol functional is used for the exchange-correlation.

	$e_{15}$	$e_{31}$	$e_{33}$
0.00 GPa	3.14	1.42	4.48
1.15 GPa	3.20	1.42	4.63
2.01 GPa	3.22	1.42	4.73

In Table 3 we summarized all the values calculated with the various functionals, also the available experimental data were given [12-14]. As shown in this table, the calculated results strongly depend on the choice of the exchange-correlation functional. Our  $e_{15}$ ,  $e_{31}$  and  $e_{33}$  values calculated with GGA functionals are in good agreement with the experimental data of Li *et al.* [12]. However, there is a significant spread between various experiments and the LDA values are consistently larger than those with GGA.

The pressure-dependency of the piezoelectric tensor is given in Table 4. Here, we calculate the piezoelectric constants for the structure optimized at fixed crystal volume, and estimate pressure by using Eq. (3). As shown in Table 4, the piezoelectric coefficient increases with pressure.

## 4. CONCLUSIONS

The structures of the PE and FE phases of  $PbTiO_3$  were investigated using the first principle quantum calculations. In the present study, under the density functional theory (DFT), various exchange-correlation functionals, such as LDA, GGA-PBE, GGA-PBEsol, GGA-AM05 were tested. All functionals predict the experimental results correctly to a certain degree, however the modified functionals for solid materials, i.e. GGA-PBEsol, GGA-AM05, yielded the structures and physical properties of  $PbTiO_3$  more reasonably than the conventional LDA and GGA-PBE functionals. In future studies, we will use GGA-PBEsol and GGA-AM05 functionals to investigate the structures and physi-

cal properties of the various piezoelectric materials such as  $PbMg_{1/3}Nb_{2/3}O_3$  (PMN),  $PbMg_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$  (PMN-PT) and  $PbIn_{1/2}Nb_{1/2}O_3$ - $PbMg_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$  (PIN-PMN-PT).

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