

# DFT INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF MODIFIED PZT

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**Abstract:** Density of states and geometrical structures of modified Lead zirconate titanate are investigated using density functional theory within local density approximation. The electronic properties and bond length variation have been studied in terms of electronic structure and bonding mechanism principles respectively. Hybridization between Ti 3d - O 2p states and ferroelectric distortion have been addressed as a theoretical approach, to rule the improvement of ferroelectric properties of Lead zirconate titanate. The analysis of Ga, Tl modified Lead zirconate titanate were found to diminish the hybridization between Ti 3d - O 2p states, the relaxed behavior lead to the reversal of the known ferroelectric distortion. Y, Ho, Yb and Lu modified Lead zirconate titanate compounds have a tendency to intense the ferroelectric stability, its exhibit higher hybridization between Ti 3d - O 2p states than pure Lead zirconate titanate, also the arrangement of the ions distortions is strongly the same as the more favoured ferroelectric states of Lead zirconate titanate.

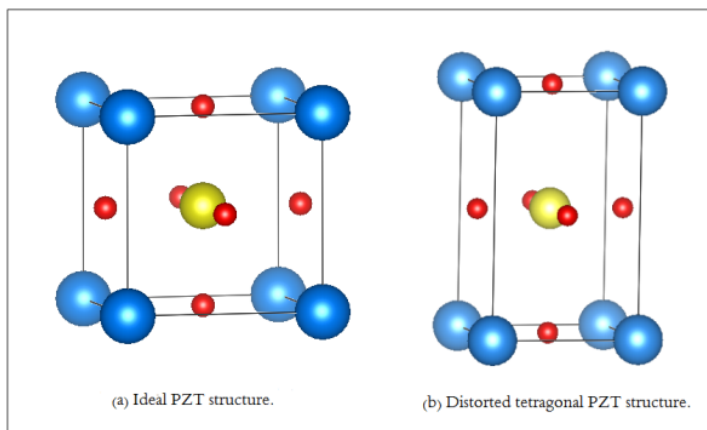
**Keywords:** DFT investigation, LDA, PZT and ferroelectricity.

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## Introduction

Due to the attractive features of Lead zirconate titanate (PZT), various theoretical and experimental studies have been reported in recent years. The high remnant polarization, high dielectric constant makes PZT one of the most widely used in many industrial applications.<sup>1-3</sup> The superior features of PZT are strongly associated with the strength of its intrinsic ferroelectric properties, thus a numerous efforts have been investigated to search the possibility of enhancing the ferroelectric properties of PZT.<sup>4-7</sup> The structure of PZT ( $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ) has the general formula  $\text{ABO}_3$ , where Pb denotes A-site, Zr or Ti denotes B-site as represented in Figure 1(a). Some kind of additives elements replace Pb ions to constitute A-site modified PZT, while some other replace Zr or Ti ions to form B-site modified PZT, the modification may include both A and B sites substitutions depending on the chemical valences of the additives ions.<sup>8</sup> In 1992, modern first-principles have been used effectively by Ronald Cohen<sup>9</sup> in order to explain the origin of ferroelectricity in perovskite oxides, the interaction between the Pb 6s and O 2p leads indirectly to increase the hybridization between Ti 3d and O 2p states, which further stabilizes the ferroelectric phase. One of striking results submitted by this work was found in the comparison between the calculated DOS of  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$ , the indirect effect of the Pb-O interaction led to shrinkage in the Ti 3d state of  $\text{PbTiO}_3$  (which is more ferroelectric) rather than Ti 3d state of  $\text{BaTiO}_3$ . Therefore, the increasing of the ferroelectric effect in perovskite structures is associated with the reduction of Ti 3d state.



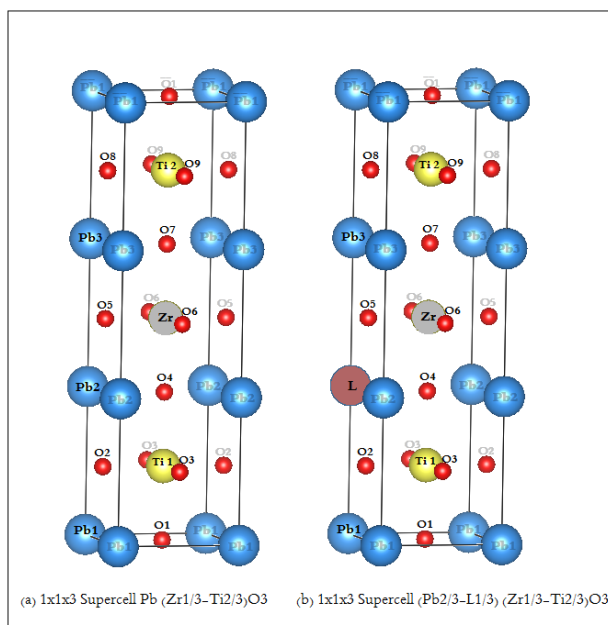
**Figure 1.** General structure of PZT. (a)- Ideal Cubic unit cell. (b) Distorted tetragonal unit cell. Where Blue spheres represent the A-site, yellow spheres represent the B-site, and red spheres represent oxygen.

The distortions of the PZT away from the ideal perovskite structure as indicated in Figure 1(b) caused by substitution technique were governed by a characteristic bonding mechanism, the B-site off-center distortions displace the center of positive charge, giving rise to spontaneous polarization, which improved the ferroelectric properties of PZT. In  $B-O_6$  octahedron which is regarded as the building block of the perovskite structure, the off-centering displaces the B-cation toward one or more oxygen ions, splitting the  $B-O_6$  into groups of short, medium and long bonds.<sup>10</sup> The occurrence of ferroelectricity in perovskite type correlated with characteristic nature of bonding lengths between A, B, O ions,<sup>11</sup> the bond lengths between A-Site and its neighboring oxygen ions determine the macroscopic properties of ferroelectric distortion. There are many reports have shown the effect of the Pb-O bond on the ferroelectric instability of PZT,<sup>12</sup> this effect made four oxygen ions (in the x-y plane) move closer to A-site, i.e A-O bond lengths are decreased in the horizontal plane. In this paper, some Pb ions are replaced by Y, Tl, Ga, Ho, Yb and Lu to build up A-site modified PZT. We investigated the proposed

modification by first principle density-functional-theory (DFT) to control ferroelectric behavior of PZT perovskite.

### Computational details

1x1x3 supercell of pure PZT were built within the framework of tetragonal symmetry space group P4mm, containing three sub cells as shown in Figure 2-(a). The B-site (Ti, Zr ions) are ordered along the [001] direction, where Ti ions are located at the center of the lower and upper sub cells while the middle sub cell containing Zr ion in the center, i.e. one Zr plane alternating with two Ti planes along [001] direction constituting  $\text{Pb}(\text{Zr}_{1/3}\text{Ti}_{2/3})\text{O}_3$  composition. The Pb ion at the middle subcell are replaced by additive elements L to obtain  $(\text{Pb}_{2/3}\text{L}_{1/3})(\text{Zr}_{1/3}\text{Ti}_{2/3})\text{O}_3$  modified PZT as shown in Figure 2-(b), L refers to Y, Tl, Ga, Ho, Yb, Lu elements. Pb 5d,6s,6p, O 2s,2p, Ti 3d,4s, and Zr 4s,4p,4d,5s orbitals have been treated as a valence orbitals. The geometry optimization and the electronic structure calculations of pure and modified PZT are carried out by Band computational program,<sup>13</sup> which exploits LDA (Local Density Approximation) based on DFT. In Band, localized atomic orbital basis sets allow for the proper modeling of periodic structures without artifacts and reduced performance arises from the artificial three-dimensional periodicity necessary in popular plane wave codes. The convergence criteria used in SCF and geometry optimization calculations is implemented by default in band as intrinsic basic step of the code procedure.



**Figure 2.** 1x1x3 Supercell of Pb (Zr<sub>1/3</sub>Ti<sub>2/3</sub>)O<sub>3</sub> and (Pb<sub>2/3</sub>L<sub>1/3</sub>) (Zr<sub>1/3</sub>Ti<sub>2/3</sub>)O<sub>3</sub> compositions.

## Results and Discussion

In order to test the modification effect on ferroelectric behavior of PZT, we made a comparison between the Ti 3d energy level in both pure and modified PZT. Figure 3 shows the DOS pattern of pure PZT which is in good agreement with the previous ab initio calculations.<sup>14</sup> Ti 3d states in Ga<sup>3+</sup>, Ti<sup>3+</sup> modified PZT are higher than in Pure PZT as shown in Figures 4(a), 4(b).

While in Y<sup>3+</sup>, Ho<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> modified PZT, It can be seen a remarkable decline in Ti 3d state as indicated in Figures 5(a), 5(b), 5(c) and 5(d). Based on the clarified basis, the shrinkage of Ti 3d state confirms the hybridization between Ti 3d-O 2p and improve the ferroelectricity of PZT. Therefore, Y<sup>3+</sup>, Ho<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>- PZT are expected to possess excellent ferroelectric properties.

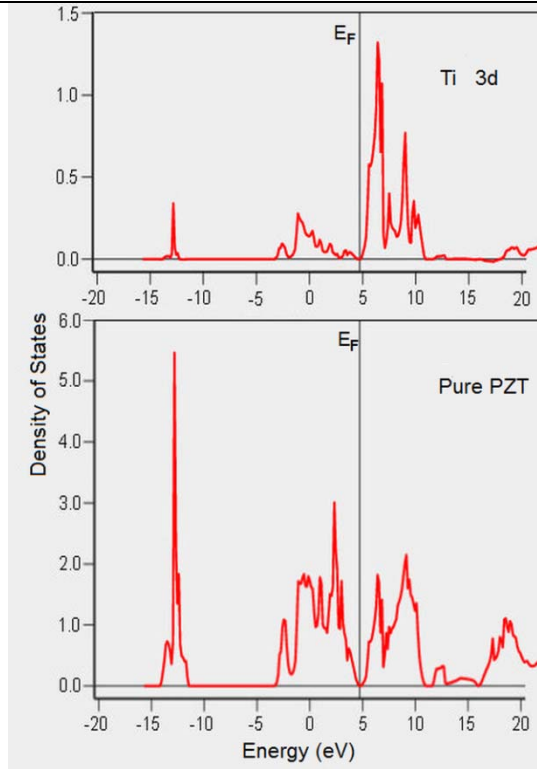


Figure 3. The calculated partial Ti 3d state and total DOS for pure PZT.

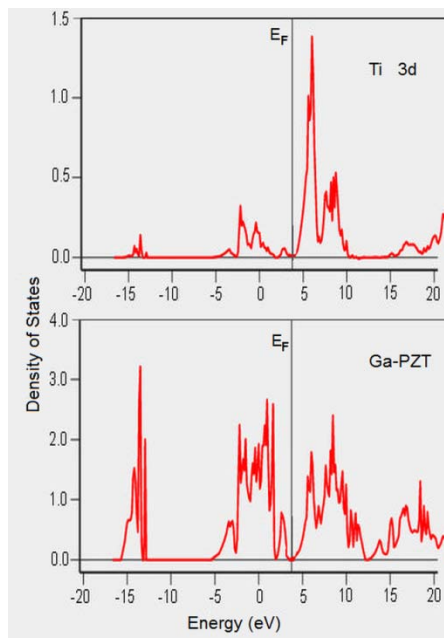
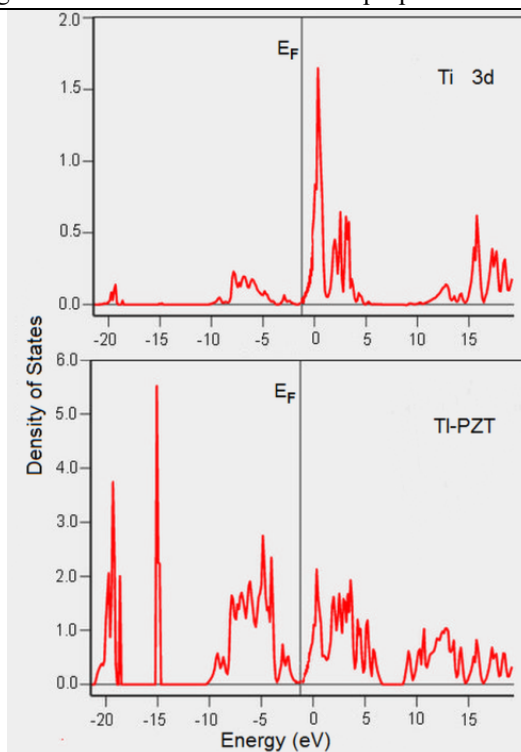


Figure 4(a). The calculated partial Ti 3d state and total DOS for Ga-PZT.



**Figure 4(b).** The calculated partial Ti 3d state and total DOS for TI-PZT.

Ti 3d states of all modified PZT types are gathered in Figure 6 to clarify differences between Ti 3d subplots caused by the effects of substitution on DOS. It's noticeable in  $Y^{3+}$ ,  $Ho^{3+}$ ,  $Yb^{3+}$ ,  $Lu^{3+}$  – PZT patterns, the conduction and valence bands shifted toward the high energy region, this is obviously because of the nature of high electrical conductivity of those additive ions, which increases of the number of electrons in PZT. While in  $Ga^{3+}$ ,  $Tl^{3+}$  – PZT despite being donor type, the DOS shifted toward the low energy region, this is due to the occurrence of hole conduction of the additive ions which known as nominally donor system.<sup>15</sup>

In the constructed supercell in Figure 2-(b), the bond lengths between A-site and oxygen ions in the x-y plane ( $O_1$ ,  $O_4$  and  $O_7$ ) were

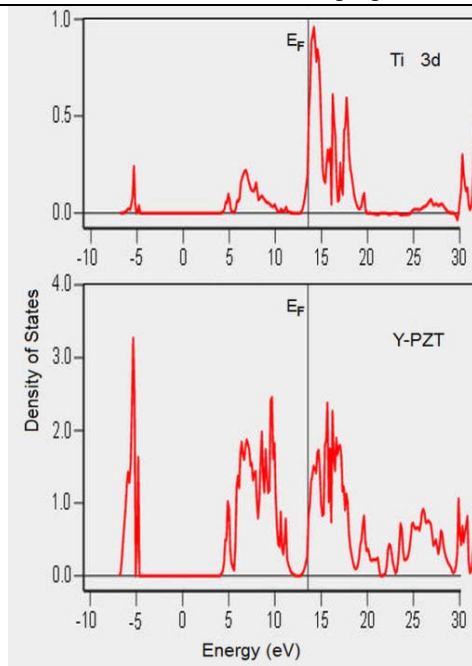
examined to demonstrate the Pb-O hybridization. In case of Ga<sup>3+</sup> Tl<sup>3+</sup>-PZT, the atomic relaxation give rise to an increase in the bond length of Pb<sub>1</sub>-O<sub>1</sub>, Ga,Tl- O<sub>4</sub>, Pb<sub>3</sub>-O<sub>7</sub> more than in pure PZT as illustrated in Table 1, which points out that the hybridization between A-site and oxygen ions is weakened. While in Y<sup>3+</sup>, Ho<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> – PZT, there is a reduction in the bond length between A-site ions and the neighboring oxygen ions located in x-y plane as illustrated in Table 2, which is an indication of strong hybridization in between A-site and O ions, this is necessary to stabilize the ionic displacement in PZT and hence improves the ferroelectric effect.

Table 3 shows the B-O bond lengths of Y<sup>3+</sup>, Ho<sup>3+</sup>, Yb<sup>3+</sup>, Lu<sup>3+</sup>-PZT. In comparison with pure PZT, the Ti ion shifted up to increase the Ti<sub>1</sub>-O<sub>1</sub> (Ti<sub>2</sub>-O<sub>7</sub>) bond and decrease the Ti<sub>1</sub>, -O<sub>4</sub> and Ti<sub>2</sub>- $\bar{O}_1$  (where  $\bar{O}_1$  is the inversion of O<sub>1</sub>), i.e. one of the two Ti–O bonds along the polar axis is the shortest, and another is the longest. Similarly, Zr-O<sub>4</sub> is increased while Zr-O<sub>7</sub> is decreased. This is a full compatibility with the familiar behavior of [001] ferroelectric distortion of high ferroelectric perovskite nature.

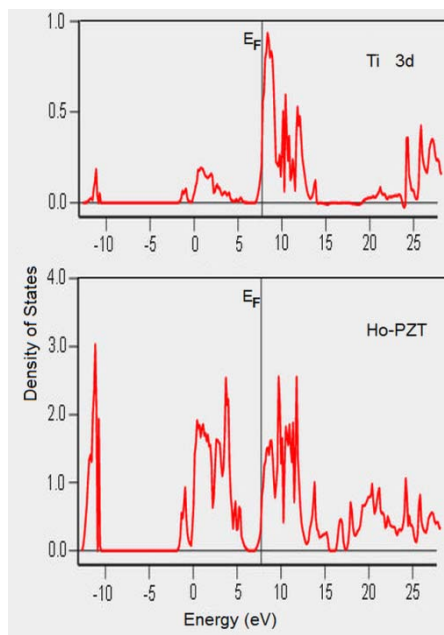
**Table 1.** Bond lengths between A-site and oxygen ions n x-y plane for Ga, Tl – PZT.

| Bond (Å)                        | Pure PZT | Ga <sup>+3</sup> - PZT | Tl <sup>+3</sup> - PZT |
|---------------------------------|----------|------------------------|------------------------|
| Pb <sub>1</sub> -O <sub>1</sub> | 2.839    | 2.888                  | 2.867                  |
| Pb <sub>2</sub> -O <sub>4</sub> | 2.839    | —                      | —                      |
| L- O <sub>4</sub>               | —        | 2.875                  | 2.872                  |
| Pb <sub>3</sub> -O <sub>7</sub> | 2.839    | 2.890                  | 2.888                  |

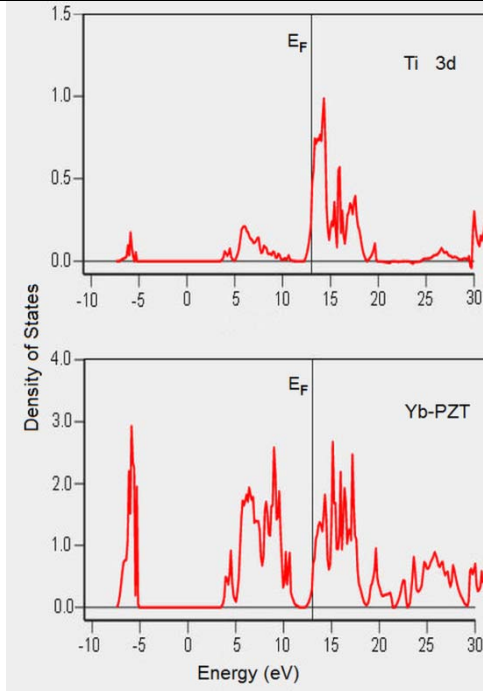




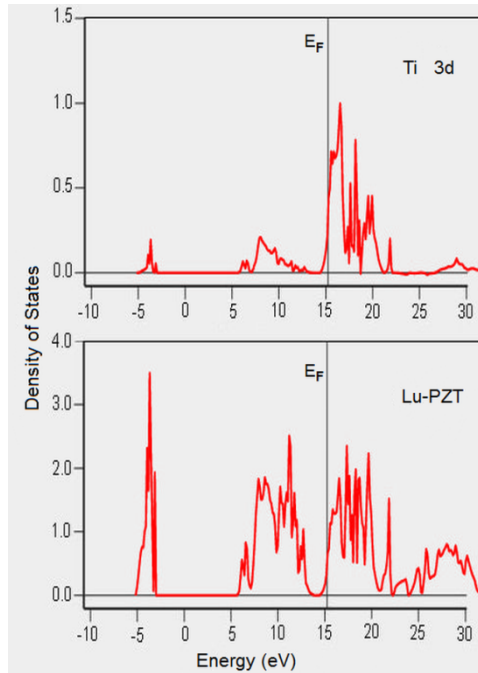
**Figure 5(a).** The calculated partial Ti 3d state and total DOS for Y-PZT.



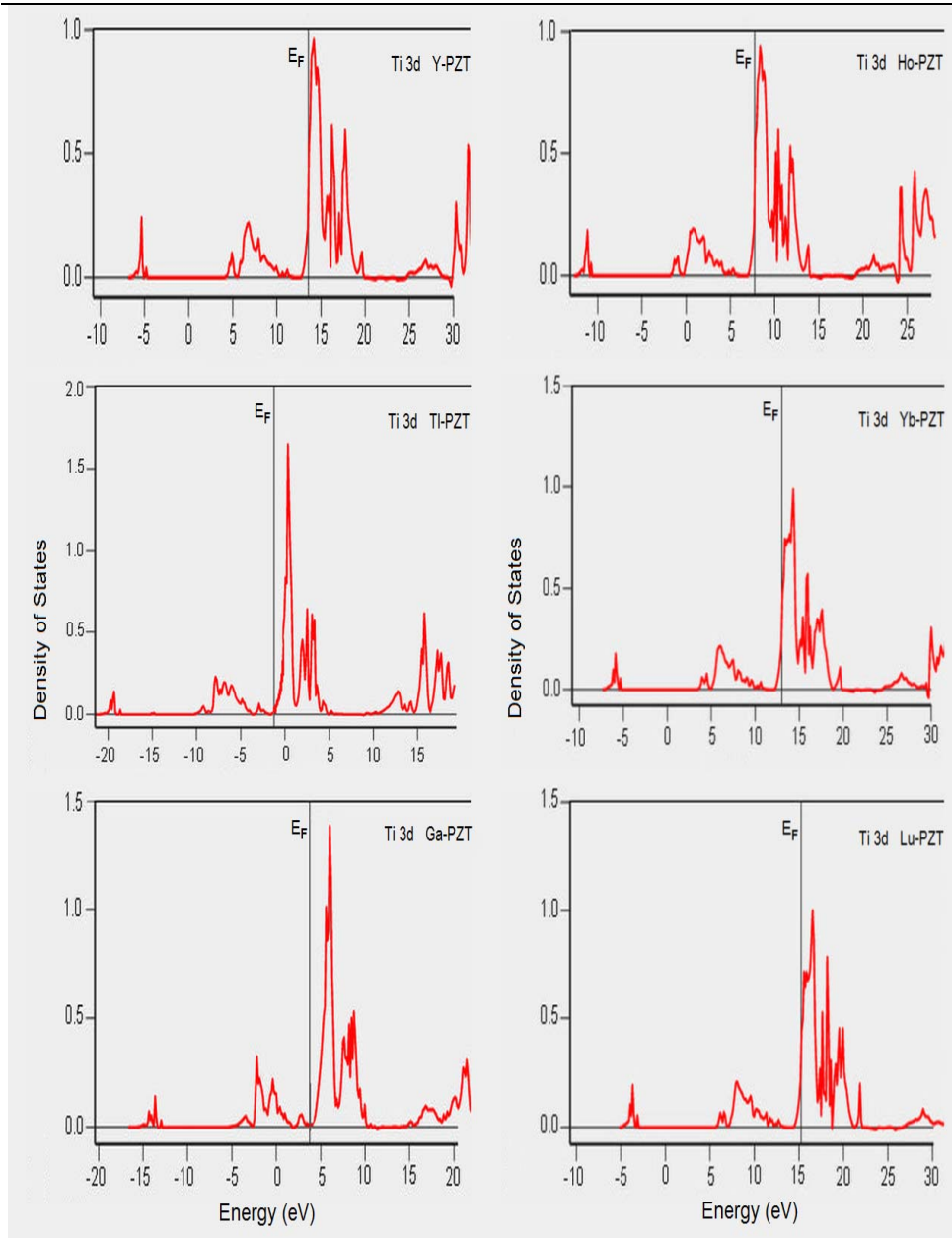
**Figure 5(b).** The calculated partial Ti 3d state and total DOS for Ho-PZT.



**Figure 5(c).** The calculated partial Ti 3d state and total DOS for Yb-PZT.



**Figure 5(d).** The calculated partial Ti 3d state and total DOS for Lu-PZT.



**Figure 6.** Ti 3d states subplots for all modified PZT types.

**Table 2.** Bond lengths between A-site and oxygen ions in x-y plane for Y, Ho, Yb and Lu – PZT.

| Bond (Å)                        | Pure PZT | Y <sup>+3</sup> -PZT | Ho <sup>+3</sup> -PZT | Yb <sup>+3</sup> -PZT | Lu <sup>+3</sup> -PZT |
|---------------------------------|----------|----------------------|-----------------------|-----------------------|-----------------------|
| Pb <sub>1</sub> -O <sub>1</sub> | 2.839    | 2.782                | 2.787                 | 2.773                 | 2.758                 |
| Pb <sub>2</sub> -O <sub>4</sub> | 2.839    | —                    | —                     | —                     | —                     |
| L- O <sub>4</sub>               | —        | 2.779                | 2.797                 | 2.773                 | 2.755                 |
| Pb <sub>3</sub> -O <sub>7</sub> | 2.839    | 2.711                | 2.781                 | 2.789                 | 2.766                 |

**Table 3.** Bond lengths between B - site and its neighboring oxygen ions for Y, Ho, Yb and Lu – PZT.

| Bond (Å)                         | Pure PZT | Y <sup>+3</sup> -PZT | Ho <sup>+3</sup> -PZT | Yb <sup>+3</sup> -PZT | Lu <sup>+3</sup> -PZT |
|----------------------------------|----------|----------------------|-----------------------|-----------------------|-----------------------|
| Ti <sub>1</sub> -O <sub>1</sub>  | 1.921    | 2.185                | 2.152                 | 2.156                 | 2.162                 |
| Ti <sub>1</sub> -O <sub>4</sub>  | 1.907    | 1.633                | 1.651                 | 1.643                 | 1.644                 |
| Ti <sub>2</sub> - O <sub>7</sub> | 1.907    | 2.299                | 2.213                 | 2.157                 | 2.142                 |
| Ti <sub>2</sub> - $\bar{O}_1$    | 1.921    | 1.855                | 1.872                 | 1.877                 | 1.878                 |
| Zr-O <sub>4</sub>                | 2.195    | 2.328                | 2.316                 | 2.218                 | 2.285                 |
| Zr- O <sub>7</sub>               | 2.195    | 2.023                | 2.019                 | 2.075                 | 2.053                 |

The recorded data in Table 4 shows the bond lengths of Ga<sup>3+</sup> Ti<sup>3+</sup>–PZT. Despite the Ti ion is shifted up, the Ti<sub>1</sub> -O<sub>1</sub> (Ti<sub>2</sub>-O<sub>7</sub>) bond is increased while Ti<sub>1</sub> -O<sub>4</sub> (Ti<sub>2</sub> - $\bar{O}_1$ ) bond is decreased (Zr-O bond changed in a similar procedure to Ti-O bond). This could be explained only when the oxygen ions disordered in contrast behavior to the previous state, i.e. oxygen ions are shifted up, which increase the bond between the B cation and the uppermost oxygen ion and decreasing the bond between B cation and the

lowermost oxygen ion. The structure of  $\text{Ga}^{3+} \text{Ti}^{3+}$ -PZT deteriorates the intrinsic ferroelectric properties of PZT.

**Table 4.** Bond lengths between B - site and its neighboring oxygen ions for Ga, Tl – PZT.

| Bond (Å)                             | Pure PZT | $\text{Ga}^{+3}$ -PZT | $\text{Ti}^{+3}$ -PZT |
|--------------------------------------|----------|-----------------------|-----------------------|
| Ti <sub>1</sub> -O <sub>1</sub>      | 1.921    | 1.725                 | 1.724                 |
| Ti <sub>1</sub> -O <sub>4</sub>      | 1.907    | 2.201                 | 2.443                 |
| Ti <sub>2</sub> - O <sub>7</sub>     | 1.97     | 1.669                 | 1.646                 |
| Ti <sub>2</sub> - $\bar{\text{O}}_1$ | 1.921    | 2.273                 | 2.291                 |
| Zr-O <sub>4</sub>                    | 2.195    | 1.845                 | 1.889                 |
| Zr- O <sub>7</sub>                   | 2.195    | 3.284                 | 2.867                 |

### Conclusions

The interplay of bonding and electronic structures of modified PZT has been studied by DFT principles calculations .The aim was to improve the ferroelectric properties of PZT, the assess identified from comparisons between pure PZT and Ga, Tl, Y, Ho, Yb, Lu modified PZT. The driving force towards our target is mainly focused on two basis: i) The ferroelectricity of perovskite structures is explained by increasing hybridization between Ti 3d - O 2p states, this hybridization confirmed by a shrinkage of Ti 3d in the computed DOS; ii) the influence of ferroelectric instability relaxation is reflected in the formation of particular distortion, this favoured distortion is characterized by particular ordering of bond lengths between A,B-sites and neighboring oxygen ions. Ga, Tl modified PZT was found to weak the hybridization between Ti 3d - O 2p state, by

rising Ti 3d state. The bond lengths between A-site and O ions in x-y plane are increased, also bond lengths between the B-site and the upper oxygen ion are increased while bond lengths between the B-site and the lower oxygen ion are decreased. These results have shown that, improvement of ferroelectricity cannot be expected in Ga, Tl modified PZT. Y, Ho, Yb, Lu modified PZT were found to support the Ti 3d - O 2p hybridization, i.e. reducing the Ti 3d states, the bond lengths between A-site and O ions in x-y plane and bond lengths between B-site and upper oxygen ion all are decreased, while bond lengths between B-site and lower oxygen ion are increased. Thus, Y, Ho, Yb, Lu enhances the ferroelectric effect of PZT.

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