Hybrid DFT calculations of the $F$ centers in cubic $\text{ABO}_3$ perovskites

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Abstract. We employed the hybrid DFT-LCAO approach as implemented in the CRYSTAL code for 135 atom supercell calculations of O vacancies with trapped electrons (known as the $F$ centers) in three cubic perovskite crystals: $\text{SrTiO}_3$, $\text{PbTiO}_3$ and $\text{PbZrO}_3$. The local lattice relaxation, charge redistribution and defect energy levels in the optical gap are compared. We demonstrate how difference in a chemical composition of host materials leads to quite different defect properties.

1. Introduction

A wide class of ternary oxides -- $\text{ABO}_3$-type perovskites -- continue to attract considerable attention as materials for solid oxide fuel cells, catalytic and electrochemical applications, hydrogen membranes, actuators, sensors, etc. [1]. For example, some of these oxides are catalytically active in the oxidation of CO and reduction of NO in automobile exhaust reduction. Mixed oxides with the $\text{ABO}_3$ perovskite structure are flexible systems as their properties can be adjusted or enhanced for specific applications by chemical doping at the A or B cation sites. Alternatively, these oxides can also contain point defects in the form of vacancies and trapped electrons/holes depending on the A,B cation- and dopant nature.

$\text{ABO}_3$ compounds comprise a rich family of crystalline structures: simple cubic (Fig.1a), tetragonal, orthorhombic, etc. which corresponds to the ferroelectric, antiferroelectric, and other phases with specific, technologically important properties. In spite of substantial efforts, the nature of defects in $\text{ABO}_3$ perovskites is poorly understood. One of the main and the most important defects is an oxygen vacancy with trapped electrons called the color $F$ center. In fact, in partly covalent perovskites these defects resemble more the $E'$ centers (Si dangling bonds) formed in several oxides and silicates, where each O ion is surrounded by only two nearest neighbor positively charged ions [2], rather than the traditional $F$ centers in MgO-type ionic solids where two electrons are strongly localized by the Madelung field in the O vacancy. However, the analogy with $E'$ centers is also incomplete since this should lead to the creation of Me–Me bonds and strong displacements of both Me ions towards each other. Thus, O vacancies in perovskites really cannot be attributed to earlier
defined types of color centers; yet for simplicity we continue to call them the $F$ centers. Detailed analysis of previous $F$ center calculations in metal oxides and perovskites is summarized in several books and review articles [1-11].

In this short paper, we present a comparative study of the $F$ centers in cubic phases of three important perovskites: SrTiO$_3$ (STO, widely used as a substrate for a growth of high-$T_c$ superconductors), PbTiO$_3$ (PTO, actuators and sonar devices) and PbZrO$_3$ (PZO, diagnostic material for radiation environment). The cubic phase is stable for STO above 105 K, whereas for PTO and PZO it is a high temperature phase. We analyze how variation in A and B cations changes properties of pure materials and defects therein. One of the main defect characteristics is the energy level position with respect to the energy bands of the pure material which controls electron/hole localization and defect stability. This means that any theoretical method used should reproduce reliably the band gap of the crystal (~3 eV in perovskites). As well known [11], standard DFT calculations strongly underestimate the band gap (by a factor of two for perovskites) whereas the Hartree-Fock method overestimates it. Our experience with perovskite calculations [12,13] demonstrates that only the hybrid functionals (B3LYP, B3PW) are able to reproduce the band gaps with high accuracy. These functionals are incorporated into the CRYSTAL code which we employed in this study (and used successfully for different material modelling [1-4]).

2. Method

Periodic structure calculations of defective cubic perovskites (Fig. 1) have been performed using the CRYSTAL code [14] with the hybrid B3PW exchange correlation functional [15] which combines the non-local exact Fock exchange and GGA exchange functionals using Becke’s three parameter method. The Gaussian-type basis sets (BSs) for Ti, Pb and O were taken from Ref. [13], while the BS for Zr was taken from [14]. The inner core electrons of Ti, Pb and Zr ions are described by Hay-Wadt effective core pseudopotentials [16]. When modeling defects, the simple cubic (high-temperature) unit cell containing one formula unit (5 atoms) was extended to a 3×3×3 supercell [9,10]. (Our calculations for orthorhombic PZO [17] do not show big differences from the cubic phase for defect structure. The effect of the supercell size was also recently analyzed in detail for the $F$ centers in STO [18].) The distance between periodically repeated defects is ~12.5 Å. Additionally, a ghost basis set of a missing O atom was centered on an O vacancy [14]. This allows us to reproduce correctly the electronic density redistribution caused by the defect.

The equilibrium geometry was obtained using analytical optimization as implemented in CRYSTAL. To get the equilibrium geometry of crystalline structure around O vacancies in cubic ABO$_3$ perovskites, the atomic sites from eight coordination spheres nearest to the $F$ center have been relaxed, keeping their spherical symmetry. The reciprocal space integration was performed by sampling the Brillouin zone with 8×8×8 and 4×4×4 Pack-Monkhorst and Gilat k-point meshes [19,20] for pure (unit cell) and defective (supercell) solids, respectively. The effective atomic charges were characterized using the static (Mulliken) population analysis rather than dynamic (Born) charges; our main interest was to analyze the charge redistribution caused by the defects.

3. Results

3.1. Perfect perovskites. The optimized cubic lattice constants $a_0$ are very close to the experimental high temperature values (Table 1) (notice that $a_0$ for PZO considerably exceeds that of the two other pervoskites). Good agreement of experimental and theoretical values is observed also for the direct band gaps. The effective Mulliken charges indicate considerable covalency of the B-O chemical bonds. There is also a weak Pb-O bonding in lead perovskites, unlike negligible Sr-O bonding in STO. The Mulliken charges show also that Sr is considerably more ionic than Pb.
**Figure 1** (Color online). (a) Unit cell of defective cubic SrTiO$_3$, (b) 3×3×3 supercell model of cubic ABO$_3$ perovskite with an O vacancy (A = Pb or Sr, B = Ti or Zr).

Table 1. The Mulliken effective atomic charges Q (in e), bond populations P (milli e), direct band gaps (eV) and lattice constants (Å) calculated for three pure ABO$_3$ perovskites. Negative bond populations mean atomic repulsion. Experimental data are given in brackets.

| Property   | PbTiO$_3$ | PbZrO$_3$ | SrTiO$_3$ |
|------------|-----------|-----------|-----------|
| Q(A)       | 1.34      | 1.30      | 1.87      |
| Q(B)       | 2.33      | 2.07      | 2.35      |
| Q(O)       | -1.23     | -1.12     | -1.41     |
| P(A-O)     | 16        | 36        | -10       |
| P(B-O)     | 98        | 100       | 88        |
| P(O-O)     | -50       | -20       | -44       |
| Band gap   | 2.87(3.40)| 3.79(3.70)| 3.63(3.75)|
| Lattice constant | 3.93(3.97)| 4.18(4.16)| 3.91(3.89)|

3.2. **Defective perovskites.** The different nature of bonding in Pb- and Sr- as well as Ti- and Zr-containing perovskites (i.e., partial Pb-O bond covalency vs. almost nominal ionic charge for Sr$^{2+}$) results in a noticeable difference in the character of relaxation around point defects and other properties. Relative outward displacements of ions surrounding the F centers from ideal crystal sites are 1 vs. 3 % for the two nearest Zr and Ti ions in defective PZO and PTO perovskites, respectively; i.e. structural sensitivity of zirconium to the presence of a vacancy is rather low. However, the inward relaxation of the eight next-nearest oxygens around the F center is markedly larger in zirconate: cf. 10 vs. 2 % for PZO and PTO, respectively, the same is true for relaxation of the next four neighboring Pb ions towards the defect: 12 vs. 5 %. These two kinds of displacements reflect a trend to maintain the Pb-O bond covalency between the relaxed atoms. At the same time, the behavior of Sr is completely
opposite to Pb, being practically indifferent to the presence of O vacancy with outward shift by 1%. However, relaxation of B (Ti, Zr) and O atoms nearest to the $F$ center in STO is closer to the relaxations in PTO than in PZO.

According to the Mulliken population analysis, the $O$ vacancy attracts $0.7\ e$, $0.9\ e$, and $1.2\ e$ from the missing O atom in PZO, PTO, and STO, respectively. Charge transfer towards two nearest Ti ions in PTO and STO is ~$0.25\ e$ larger than to Zr ions in PZ, mainly due to a higher covalency of the Ti-O bond as compared to Zr-O. Simultaneously, the ionicity of O atoms in STO is ~$0.2$-$0.3\ e$ higher than those in PTO and PZ, due to partial covalency of the Pb-O bonds. This is well confirmed by a comparative analysis of the difference electron densities plotted in Fig.2, which clearly demonstrates involvement of Pb, Zr and Ti ions in the defect-changed bond covalency with oxygens whereas Sr ions are practically indifferent to defect-induced changes.

The calculated band structures for the cubic PZO, PTO, and STO containing $F$ centers (Table 2 and Fig.3) also show differences between the $F$ centers. The $F$ center in PZO is a deep defect, with the donor level close to the middle of the gap, $1.7\ eV$ below the bottom of conduction band (CB). The defect energy band caused by the interaction of periodically repeated defects has a small dispersion over the Brillouin zone (0.14 eV). In contrast, in PTO and STO titanates, the defect level is much closer to the CB bottom, characterized by a larger dispersion. As to defect formation energy, it is noticeably larger for STO than for PZO and PTO.

Table 2. Comparative analysis of main properties of defective PbTiO$_3$, PbZrO$_3$, and SrTiO$_3$ perovskites. $\Delta \epsilon_{db\text{-}gap}$ is distance from the conduction band bottom (CB), $\delta$ the defect band dispersion, $E_{\text{form}}^\Gamma(F)$ the formation energy.

| Perovskite | Atoms of perovskite nearest to vacancy | Mulliken charge, e\(^\dagger\) | Parameters of defect level, eV | $E_{\text{form}}^\Gamma(F)$, eV |
|------------|---------------------------------------|------------------------------|--------------------------------|--------------------------|
|            | perfect crystal                       | defective crystal            | $\Delta \epsilon_{db\text{-}gap}$ | $\delta$ |                      |
| PbTiO$_3$  | $F$ center$^{a)}$                      | 2.33                         | 2.32                           | -1.23                  | 0.96                | 0.21                | 7.82                |
|            | Ti                                    | 1.34                         | 1.25                           |                        |                      |                      |                    |
|            | O                                     |                              |                                |                        |                      |                      |                    |
|            | Pb                                    |                              |                                |                        |                      |                      |                    |
| PbZrO$_3$  | $F$ center$^{a)}$                      | 2.07                         | 2.09                           | -1.12                  | 1.71                | 0.14                | 7.25                |
|            | Zr                                    |                              |                                |                        |                      |                      |                    |
|            | O                                     |                              |                                |                        |                      |                      |                    |
|            | Pb                                    |                              |                                |                        |                      |                      |                    |
| SrTiO$_3$  | $F$ center$^{a)}$                      | 2.35                         | 2.34                           | -1.41                  | 0.69                | 0.25                | 8.74                |
|            | Ti                                    |                              |                                |                        |                      |                      |                    |
|            | O                                     |                              |                                |                        |                      |                      |                    |
|            | Sr                                    |                              |                                |                        |                      |                      |                    |

$^a)$$^a)An excess of the electron density with respect to an empty vacancy.
Figure 2 (Color online). Charge redistribution around the $F$ center in PbTiO$_3$ (a), PbZrO$_3$ (b), and SrTiO$_3$ (c): the total density in the perfect bulk perovskite minus the sum of electronic densities of both lattice of oxygen atoms positioned in vacancy sites and defective perovskite. Dash-dot (black) isolines correspond to the zero level. Dashed (blue) isolines stand for a decrease in the electron density and solid (red) lines for an increase.

Figure 3 (Color online). The DOS and band structure of the defective PbTiO$_3$ (a), PbZrO$_3$ (b), and SrTiO$_3$ (c). Orange line inside the band gap is the defect band.
4. Conclusions

The CRYSTAL code with hybrid exchange correlation functionals combined with the supercell model is an excellent tool which permits a detailed study of the point defects in partly covalent materials, including the ionization energies of shallow donors which control material conductivity and defect stability. Thus, the results obtained here for three types of defective cubic ABO₃ perovskites show a strong defect property dependence on the chemical nature of A and B atoms: the same F centers could be deep defects in PbZrO₃ and shallow in PbTiO₃ and SrTiO₃.

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