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## ABO<sub>3</sub> perovskite as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and surface F-center first principles predictions

Roberts Eglitis , J. Purans , A. I. Popov  and S. Piskunov   
*Institute of Solid State Physics, University of Latvia,  
8 Kengaraga Str., Riga LV1063, Latvia  
\*rieglitis@gmail.com*

Ran Jia   
*Laboratory of Theoretical and Computational Chemistry,  
Institute of Theoretical Chemistry,  
Jilin University, Changchun 130023, China  
jiaran@jlu.edu.cn*

S. P. Kruchinin   
*Bogolyubov Institute for Theoretical Physics,  
NASU, 03143 Kyiv, Ukraine; University of Leipzig,  
Felix Bloch Institute for Solid State Physics,  
04103 Leipzig, Germany  
sergeikruchinin@yahoo.com*

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We, at the *ab initio* level, simulated the rearrangement magnitudes of the adjacent neighboring ions, surrounding the (100) surface F-center in ABO<sub>3</sub> perovskite matrixes. They are noticeably greater than the respective ionic shift magnitudes of the adjacent neighboring ions surrounding the bulk F-center. In ABO<sub>3</sub> perovskites, the electron charge is noticeably better bounded on the inside of the bulk oxygen vacancy, as interior the respective (100) surface vacancy. The oxygen vacancy formation energy, located on the (100) surface of ABO<sub>3</sub> perovskites, as a rule, is smaller as in the bulk. This slight energy distinction encourages the oxygen vacancy segregation from the ABO<sub>3</sub> perovskite bulk to their (100) surfaces. The ABO<sub>3</sub> complex oxide (100) surface F-center generated defect levels are positioned nearer to the (100) surface CB bottom than the bulk F-center generated respective defect levels. In contrary, the BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub>, both, surface and bulk F-center charges are well localized inside the fluorine vacancy. The ionic rearrangement magnitudes of the adjacent neighboring ions, surrounding the surface and bulk F-centers in BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> matrixes, are much smaller regarding the respective situation in ABO<sub>3</sub> perovskites.

*Keywords:* *Ab initio* computations; F-center; oxygen vacancy; ABO<sub>3</sub> perovskites; defects; BaF<sub>2</sub>.

\*Corresponding author.

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## 1. Introduction

Different aspects of  $ABO_3$  perovskite (100) surfaces as well as their (100) heterostructures are very hot topics in modern condensed matter physics.<sup>1–17</sup>  $SrTiO_3$  (STO) is frequently utilized for substrates of superconducting thin films.<sup>18</sup> The perfect energy band structure as well as suitable light absorption, combined with increased carrier disconnection of  $TiO_2/SrTiO_3$  heterojunction promote the creation of reactive bactericidal oxygen species.<sup>19</sup>  $BaTiO_3$  (BTO) is used in multiple technological implementations, for example, as transducers, sensors and multilayer capacitors.<sup>20–22</sup> Recently, the multilayered  $TiO_2/BaTiO_3/Au$  heterostructured nanorod arrangement was successfully synthesized for the improvement of photo-dynamic work as an antibacterial coating.<sup>23</sup>  $PbZrO_3$  perovskite has a huge implementation potential in power generators as well as in energy storage capacitors.<sup>24</sup>  $SrZrO_3$  complex oxide material is an attractive candidate for a huge variety of optoelectronic applications.<sup>25</sup> Barium fluoride ( $BaF_2$ ) is frequently used as a viewport window for implementations in thermography.<sup>26</sup> Strontium fluoride ( $SrF_2$ ) is an optical material.  $SrF_2$  is used as a thermoluminescent dosimeter crystal as well as the optical coating on lenses.<sup>27</sup> Finally, calcium fluoride ( $CaF_2$ ) is widely used as the flux in the aluminum industry.<sup>28</sup>

The  $F$ -center resonance in  $CaF_2$  matrix has been experimentally detected by Arends<sup>29</sup> and well correlated with the optical absorption band located at 3.3 eV. According to experimental measurements performed by Nepomnyashchikh *et al.*,<sup>30</sup> the X-ray irradiation of undoped  $BaF_2$  crystal at 77 K temperature creates the  $F$ -centers having optical absorption band located at 2.3 eV.<sup>30</sup> Lastly, the experimentally detected  $F$ -center absorption energy in the  $SrF_2$  matrix at very low 4 K temperature is situated at 2.85 eV.<sup>31</sup> It is well known that nowadays the defect engineering is a very efficient approach to manipulate the physical properties of different technologically relevant materials.<sup>32–35</sup> Oxygen vacancy ( $V_O$ ) in the  $ABO_3$  perovskites traps two electrons.<sup>36</sup>  $V_O$  is the most frequent classical point defect in the  $ABO_3$  perovskites and it is denoted in the scientific literature as the  $F$ -center. The  $F$ -center in  $BaF_2$ ,  $SrF_2$  and  $CaF_2$  matrixes is a single electron trapped inside the anion vacancy.<sup>37–39</sup>

Strontium titanate (STO) is the centrosymmetric paraelectric and cubic material at room temperature (RT).<sup>40</sup> STO has the symmetry group ( $Pm\bar{3}m$ ) and the symmetry group number 221. Exactly the same symmetry group ( $Pm\bar{3}m$ ) as well as the symmetry group number 221 in the cubic phase have also another  $ABO_3$  perovskites, including our studied  $BaTiO_3$ ,  $SrZrO_3$  and  $PbZrO_3$  matrixes. STO and another our computed  $ABO_3$  perovskites have 5 atoms in the primitive cell.<sup>41</sup> Namely, the Sr ion is located at the corner of the cubic unit cell with the following coordinates (0, 0, 0). The O ions are located at the face centers of the cube with the subsequent coordinates (0.5, 0.5, 0), (0.5, 0, 0.5), (0, 0.5, 0.5). Lastly, the Ti ion is located at the center of the cubic unit cell with the consecutive coordinates (0.5, 0.5, 0.5). Another class of our computed materials  $SrF_2$ ,  $BaF_2$  and  $CaF_2$  cubic unit cell contains three atoms.

*ABO<sub>3</sub> perovskite as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and surface F-center*

One cation (Sr, Ba or Ca) is chosen as the coordinate origin in our computations (0, 0, 0) as well as two anions are located at the following coordinates (1/4a, 1/4a, 1/4a) and (3/4a, 3/4a, 3/4a). There  $a$  is the SrF<sub>2</sub>, BaF<sub>2</sub> and CaF<sub>2</sub> bulk lattice constant. All our computed SrF<sub>2</sub>, BaF<sub>2</sub> and CaF<sub>2</sub> matrixes are the cubic ( $Fm\bar{3}m$ ) large bandgap insulators. All of them have the 225 symmetry group number.<sup>42</sup> The BaTiO<sub>3</sub> perovskite has several phase transitions. Namely, the BaTiO<sub>3</sub> matrix structure changes<sup>43</sup> from rhombohedral ( $R3m$ ) structure to orthorhombic ( $Amm2$ ) structure at 183 K temperature. At 278 K temperature, the BaTiO<sub>3</sub> structure changes to tetragonal phase ( $P4mm$ ). Finally, at 403 K temperature, the BaTiO<sub>3</sub> structure changes to cubic phase ( $Pm\bar{3}m$ ). In the SrZrO<sub>3</sub> perovskite matrix we observed three phase transitions.<sup>44,45</sup> SrZrO<sub>3</sub> is at orthorhombic phase ( $Pnma$ ) from the room temperature till a temperature of 995 K.<sup>44,45</sup> From 995 K till 1105 K, SrZrO<sub>3</sub> is in another orthorhombic phase with different symmetry group number ( $Cmcm$ ).<sup>44,45</sup> From 1105 K till 1440 K temperatures, SrZrO<sub>3</sub> is in the tetragonal phase ( $I4/mcm$ ). Finally, at temperatures above 1440 K, SrZrO<sub>3</sub> has the cubic structure with the symmetry group ( $Pm\bar{3}m$ ).

The objectives of research, described in this contribution, was to carry out the required additional *ab initio* B3PW computations, in order to finish our long lasting work, dealing with the  $F$ -centers in PbZrO<sub>3</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, SrF<sub>2</sub>, CaF<sub>2</sub> and BaF<sub>2</sub> matrixes. After finishing our *ab initio* B3PW computations for the  $F$ -centers in BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, SrZrO<sub>3</sub>, PbZrO<sub>3</sub> perovskites as well as SrF<sub>2</sub>, BaF<sub>2</sub> and CaF<sub>2</sub> fluorides, we carefully analyzed systematic tendencies of the  $F$ -center behavior, and summarized them in a way conveniently accessible for readers.

## 2. Computational Method

We carried out our first-principles simulations for the  $F$ -centers in the PbZrO<sub>3</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> perovskites as well as SrF<sub>2</sub>, BaF<sub>2</sub> and CaF<sub>2</sub> fluorides using the brilliant CRYSTAL<sup>46</sup> computer package. In our numerical simulations, we employed the well-known hybrid exchange-correlation functional B3PW.<sup>47,48</sup> The world famous CRYSTAL computer program package<sup>46</sup> utilizes the Gaussian-type basis sets.<sup>49</sup> In our *ab initio* simulations, each atom in PbZrO<sub>3</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> and CaF<sub>2</sub> compounds have the localized basis sets.<sup>46</sup> In our first principles simulations for the SrZrO<sub>3</sub>, PbZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> perovskites, containing the  $F$ -center defect, for Sr, Ba, Pb, Ti and O atoms, we employed the basis sets developed by Piskunov *et al.*<sup>49</sup> Our used atomic basis sets for SrF<sub>2</sub>, CaF<sub>2</sub> and BaF<sub>2</sub> matrixes are described in Refs. 37–39. Finally, for the Zr atom, we employed the Zr basis set from the CRYSTAL code home page.<sup>46</sup> In our *ab initio* computations, we carried out the reciprocal space integration by sampling the Brillouin zone of the PbZrO<sub>3</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> and CaF<sub>2</sub> unit cell by the  $8 \times 8 \times 8$  times expanded Pack-Monkhorst<sup>50</sup> mesh. We performed bulk  $F$ -center *ab initio* computations in SrZrO<sub>3</sub>, PbZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> matrixes employing the  $3 \times 3 \times 3$  times expanded supercells containing 135 atoms (Fig. 1).

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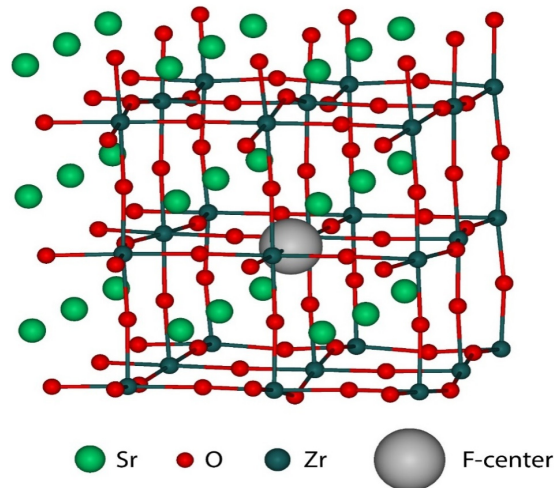


Fig. 1. (Color online) Depiction of our computed  $\text{SrZrO}_3$  cubic supercell, with  $3 \times 3 \times 3$  extension, containing the  $F$ -center.

Thereby, in our *ab initio* bulk  $F$ -center computations in  $\text{ABO}_3$  perovskites, the supercell consisted from 134 atoms as well as the single  $F$ -center (Fig. 1).

In order to simulate the  $F$ -center, located on the  $\text{ZrO}_2$ -terminated  $\text{SrZrO}_3$  (001) surface (Fig. 2), we used the two-dimensional slab model, which contained 11 layers.<sup>51</sup> In our *ab initio*  $\text{ZrO}_2$ -terminated  $\text{SrZrO}_3$  (001) surface  $F$ -center simulations, we employed the  $3 \times 3 \times 1$  times expanded surface supercells. For  $\text{SrZrO}_3$ ,  $\text{PbZrO}_3$  and  $\text{SrTiO}_3$  perovskites, we computed the  $F$ -center located on  $\text{ZrO}_2$  or  $\text{TiO}_2$ -terminated (001) surfaces. In contrast, for the  $\text{BaTiO}_3$  matrix, we computed the  $F$ -center located on the  $\text{BaO}$ -terminated (001) surface (Fig. 3).<sup>52</sup> For the  $F$ -center computations, located on the  $\text{BaO}$ -terminated BTO (001) surface, we

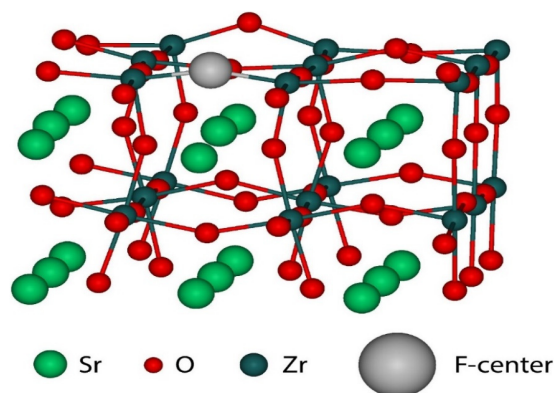


Fig. 2. (Color online) Depiction of the single  $F$ -center containing  $\text{ZrO}_2$ -terminated  $\text{SrZrO}_3$  (001) surface atomic structure.

*ABO<sub>3</sub> perovskite as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and surface F-center*

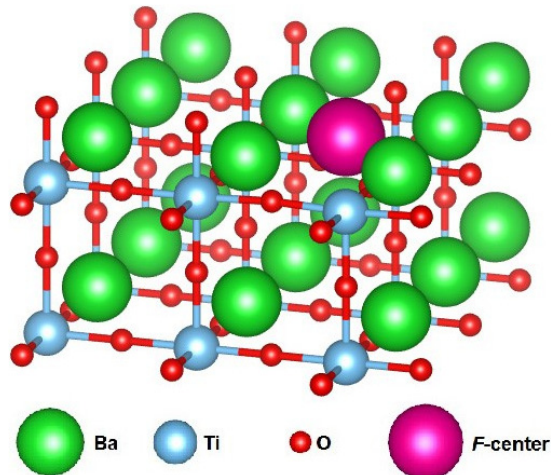


Fig. 3. (Color online) Depiction of the single  $F$ -center containing BaO-terminated BaTiO<sub>3</sub> (001) surface atomic structure.

used the  $3 \times 3 \times 1$  extension of the BTO (001) surface supercells. Our computed BTO (001) slab consisted from 11 layers. Thereby, in our *ab initio* computations, we employed the BTO slab consisting of 242 atoms as well as the single  $F$ -center, positioned on the BaO-terminated BaTiO<sub>3</sub> (001) surface (Fig. 3).<sup>52–55</sup> In order to compute the  $F$ -center defect, we used the 48-atom CaF<sub>2</sub> supercell (Fig. 4). We removed one of the fluorine atoms in the CaF<sub>2</sub> matrix, as depicted in Fig. 4. As a

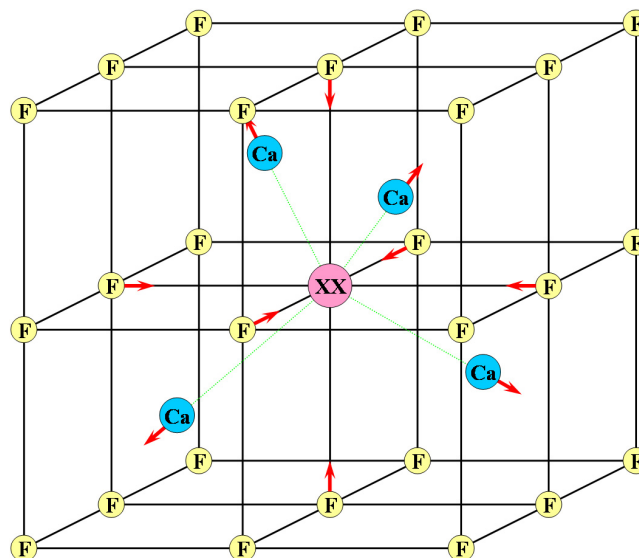


Fig. 4. (Color online) Depiction of the single  $F$ -center (XX) in the CaF<sub>2</sub> matrix and its nearest neighbor surrounding atoms.

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next step, we added the basis set centered at the fluorine vacancy in the  $\text{CaF}_2$  matrix, corresponding to the so-called “ghost” atom. This allows to obtain as good as possible description of the  $F$ -center in  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  matrixes.

### 3. *Ab initio* Computation Results

As a starting point of our *ab initio* B3PW computations, we computed the  $\text{SrZrO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbZrO}_3$  and  $\text{SrTiO}_3$  perovskite as well as  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$  fluoride bulk lattice constants. Our *ab initio* B3PW computed  $\text{SrZrO}_3$  bulk lattice constant ( $a_0$ ) 4.163 Å is almost in a perfect agreement with the experimentally at 1423 K temperature measured  $\text{SrZrO}_3$  cubic structure lattice constant 4.154 Å.<sup>56</sup> Also, our *ab initio* B3PW computed  $\text{BaTiO}_3$  bulk lattice constant 4.007 Å is in a fine agreement with the experimentally measured  $\text{BaTiO}_3$  lattice constant in a cubic phase equal to 4.00 Å.<sup>57</sup> The same, also our *ab initio* B3PW computed  $\text{PbZrO}_3$  bulk lattice constant, equal to 4.177 Å, is in a fair agreement with the experimentally detected respective  $\text{PbZrO}_3$  lattice constant in a cubic phase, measured at 520 K temperature — 4.1614 Å.<sup>58</sup> Finally, our *ab initio* B3PW computed  $\text{SrTiO}_3$  bulk lattice constant 3.904 Å is in almost ideal coincidence with the experimentally measured  $\text{SrTiO}_3$  lattice constant in the cubic structure equal to 3.89845 Å at 110 K temperature<sup>59</sup> (Table 1). Also, for  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$  fluorides, our *ab initio* B3PW computed bulk lattice constants (6.26 Å, 5.845 Å and 5.50 Å, respectively) are in a good agreement with the available experimental data (6.20 Å,<sup>60</sup> 5.799 Å,<sup>61</sup> 5.46 Å,<sup>62</sup> respectively) (Table 1).

Our *ab initio* B3PW computed  $\text{SrZrO}_3$  bulk  $\Gamma$ - $\Gamma$  bandgap is equal to exactly 5.00 eV for the pristine  $\text{SrZrO}_3$  crystal, whereas the *ab initio* computed  $\text{SrZrO}_3$   $\Gamma$ - $\Gamma$  bulk bandgap for the  $F$ -center defect containing  $\text{SrZrO}_3$  crystal is slightly larger and equal to 5.07 eV. The experimentally measured  $\text{SrZrO}_3$  bulk  $\Gamma$ - $\Gamma$  band gap is available only in the orthorhombic phase (5.6 eV),<sup>63</sup> stable at RT. Our *ab initio* B3PW computed  $\text{BaTiO}_3$  bulk  $\Gamma$ - $\Gamma$  bandgap is equal to 3.55 eV (Table 2). The single  $F$ -center defect containing  $\text{BaTiO}_3$  bulk  $\Gamma$ - $\Gamma$  bandgap is slightly larger (3.58) eV. According to the experiments, performed by Wemple,<sup>64</sup>  $\text{BaTiO}_3$  bulk  $\Gamma$ - $\Gamma$  bandgap at RT is equal to 3.38 or 3.27 eV for light polarized parallel or perpendicular, respectively, to the ferroelectric axis  $c$ . Our *ab initio* B3PW computed  $\text{PbZrO}_3$  bulk X-X bandgap is equal to 3.79 eV. It is in good agreement with the experimentally detected<sup>65</sup>  $\text{PbZrO}_3$  bandgap in the RT at orthorhombic phase 3.7 eV.<sup>65</sup> The B3PW

Table 1. *Ab initio* B3PW computed and experimental  $\text{SrZrO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbZrO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$  bulk lattice constants (in Å).

Material	$\text{SrZrO}_3$	$\text{BaTiO}_3$	$\text{PbZrO}_3$	$\text{SrTiO}_3$	$\text{BaF}_2$	$\text{SrF}_2$	$\text{CaF}_2$
Functional	B3PW	B3PW	B3PW	B3PW	B3PW	B3PW	B3PW
Theory	4.163	4.007	4.177	3.904	6.26	5.845	5.50
Experiment	4.154	4.00	4.1614	3.89845	6.20	5.799	5.46
	Ref. 56	(Ref. 57)	(Ref. 58)	(Ref. 59)	(Ref. 60)	(Ref. 61)	(Ref. 62)

*ABO<sub>3</sub> perovskite as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and surface F-center*

Table 2. *Ab initio* B3PW computed and experimental SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, PbZrO<sub>3</sub>, CaF<sub>2</sub>, BaF<sub>2</sub> and SrF<sub>2</sub> as well as *F*-center defect containing bulk bandgaps (in eV).

Material	SrZrO <sub>3</sub>	BaTiO <sub>3</sub>	PbZrO <sub>3</sub>	CaF <sub>2</sub>	BaF <sub>2</sub>	SrF <sub>2</sub>
Bandgap	5.00	3.55	3.79	10.96	11.30	11.31
Gap with <i>F</i> -center	5.07	3.58	3.97	10.99	11.28	11.34
Experiment	5.6 (Ref. 63) (Orthorhombic phase)	3.38; 3.27 (Ref. 64) (Tetragonal ↔ Orthorhombic)	3.7 (Ref. 65) (Orth. Phase)	12.1 (Ref. 66)	11.00 (Ref. 66)	11.25 (Ref. 66)

computed X-X band gap for PbZrO<sub>3</sub> bulk, containing the *F*-center defect, is equal to 3.97 eV (Table 2). Our *ab initio* B3PW computed bulk  $\Gamma$ - $\Gamma$  bandgap value for CaF<sub>2</sub> (10.96 eV) is by 1.14 eV underestimated regarding the experimental value (12.1 eV)<sup>66</sup> (Table 2). The  $\Gamma$ - $\Gamma$  bulk bandgap for the CaF<sub>2</sub> fluoride, containing the *F*-center defect, is equal to 10.99 eV (Table 2). The B3PW computed BaF<sub>2</sub> bulk bandgap at  $\Gamma$ -point is equal to 11.30 eV, whereas the bandgap at the same  $\Gamma$ -point for BaF<sub>2</sub> fluoride containing the *F*-center defect is equal to 11.28 eV. The experimentally measured BaF<sub>2</sub> direct bandgap at  $\Gamma$ -point is equal to 11.00 eV.<sup>66</sup> Finally, our *ab initio* B3PW computed SrF<sub>2</sub> bulk  $\Gamma$ - $\Gamma$  bandgap is equal to 11.31 eV, whereas the bandgap for the SrF<sub>2</sub> matrix containing the *F*-center is larger by 0.03 eV and equal to 11.34 eV. The experimental SrF<sub>2</sub> optical bulk band gap is equal to 11.25 eV,<sup>66</sup> almost in a perfect agreement with our *ab initio* B3PW computation result.

As we can see from the Table 2 and Fig. 5, our *ab initio* B3PW computed SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, PbZrO<sub>3</sub>, CaF<sub>2</sub>, BaF<sub>2</sub> and SrF<sub>2</sub> bulk bandgaps always are in a fair agreement with the available experimental data. The largest difference between our *ab initio* B3PW computed CaF<sub>2</sub> bulk  $\Gamma$ - $\Gamma$  bandgap (10.96 eV) as well as experimentally

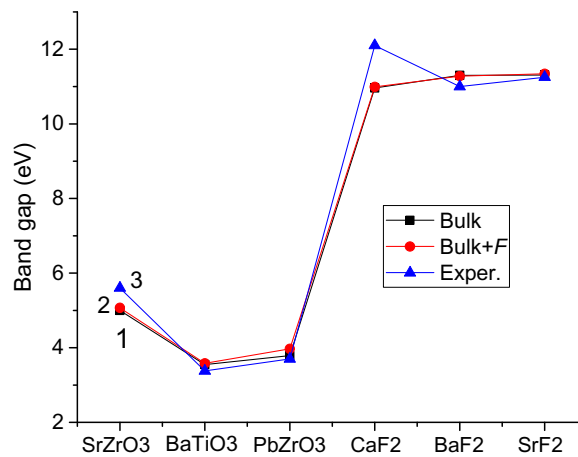


Fig. 5. (Color online) Our *ab initio* B3PW computed SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, PbZrO<sub>3</sub>, CaF<sub>2</sub>, BaF<sub>2</sub> and SrF<sub>2</sub> direct bulk bandgap value (1), direct bulk bandgap value containing the single *F*-center defect (2) as well as the experimental  $\Gamma$ - $\Gamma$  bandgap (3) (in eV).

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measured direct  $\text{CaF}_2$  bulk bandgap at  $\Gamma$ -point (12.1 eV Ref. 66) is for the  $\text{CaF}_2$  fluoride (1.14 eV) (Table 2 and Fig. 5). In contrast, the difference between our *ab initio* B3PW computed  $\text{SrF}_2$  bulk bandgap at  $\Gamma$ -point (11.31 eV) as well as the respective experimental bandgap (11.25 eV) is only 0.06 eV (Table 2). It is worth to note, that according to our *ab initio* B3PW computations, the  $F$ -center defect containing  $\text{SrZrO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbZrO}_3$ ,  $\text{CaF}_2$  and  $\text{SrF}_2$  direct bulk bandgaps are slightly larger than the respective bulk bandgaps for the pristine materials (Table 2 and Fig. 5). The single exception from this systematic trend is our *ab initio* B3PW computed  $\Gamma$ - $\Gamma$  bandgap for the perfect  $\text{BaF}_2$  bulk (11.30 eV) (Table 2 and Fig. 5), which is 0.02 eV larger than the respective  $\Gamma$ - $\Gamma$  bandgap for the  $\text{BaF}_2$  fluoride containing the  $F$ -center defect. As a next step, we performed the relaxation of nearest neighbor atoms, surrounding the  $F$ -center defect in  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$  matrixes (Table 3). As we can see from Table 3, for all three our *ab initio* B3PW computed  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$  fluorides, the fluorine atom F is attracted towards the bulk  $F$ -center by ( $-0.23\%$ ,  $-0.27\%$  and  $-0.28\%$  of the  $a_0$ , respectively). The displacement magnitudes of Ba, Sr and Ca atoms are considerable smaller ( $+0.03\%$ ,  $-0.02\%$  and  $+0.15\%$  of  $a_0$ , respectively). The Ba and Ca atoms are repulsed from the bulk  $F$ -center, whereas the Sr atom, by a very small magnitude ( $-0.02\%$  of  $a_0$ ), is attracted towards the  $\text{SrF}_2$  fluoride bulk  $F$ -center (Table 3).

It is worth to note that in the case of the (111) surface  $F$ -center in the  $\text{BaF}_2$  fluoride, the nearest neighbor atom displacement magnitudes are slightly larger than it was for the bulk  $F$ -center in the  $\text{BaF}_2$  matrix (Table 3). Namely, the nearest Ba atoms are attracted towards the (111) surface  $F$ -center in the  $\text{BaF}_2$  fluoride by ( $-0.13\%$  of the  $a_0$ ).

Also, the next nearest neighbor F atoms in  $\text{BaF}_2$  are attracted towards the (111) surface  $F$ -center by approximately 1.5 times larger relaxation magnitude ( $-0.37\%$  of  $a_0$ ) than it was in the  $\text{BaF}_2$  bulk  $F$ -center case ( $-0.23\%$  of  $a_0$ ) (Table 3).

As we can see from Table 4, the nearest neighbor B atoms always are repulsed from the bulk  $F$ -center in  $\text{SrZrO}_3$ ,  $\text{PbZrO}_3$ ,  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  matrixes.<sup>67-75</sup> The B atom repulsion displacement magnitudes are quite different, ranging from only ( $+0.48\%$  of  $a_0$ ) in the  $\text{PbZrO}_3$  perovskite till ( $+7.76\%$  of  $a_0$ ) in  $\text{SrTiO}_3$  (Table 4). Just opposite, the second nearest neighbor O atoms, according to our *ab initio* B3PW

Table 3. Our *ab initio* B3PW computed relaxation of ten nearest atoms surrounding the bulk  $F$ -center defect in  $\text{BaF}_2$ ,  $\text{SrF}_2$  and  $\text{CaF}_2$  matrixes (in % of bulk lattice constant  $a_0$ ).

Material	<i>n</i> th nearest	Atom	Number	B3PW $\Delta z$ (%)
$\text{BaF}_2$	1	Ba	4	+0.03
	2	F	6	-0.23
$\text{SrF}_2$	1	Sr	4	-0.02
	2	F	6	-0.27
$\text{CaF}_2$	1	Ca	4	+0.15
	2	F	6	-0.28



*ABO<sub>3</sub> perovskite as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and surface F-center*

Table 4. Our *ab initio* B3PW computed three nearest neighbor atom displacements around the bulk *F*-center located in the SrZrO<sub>3</sub>, PbZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> matrixes (% of  $a_0$ ).

Material	SrZrO <sub>3</sub>	PbZrO <sub>3</sub>	BaTiO <sub>3</sub>	SrTiO <sub>3</sub>
B atom displ.	+3.68	+0.48	+1.06	+7.76
O atom displ.	-2.63	—	-0.71	-7.79
A atom displ.	+0.46	-5.99	-0.08	+3.94

computations, always are attracted towards the bulk *F*-center. The largest O atom displacement magnitude, towards the bulk *F*-center, again is in the SrTiO<sub>3</sub> perovskite (-7.79% of  $a_0$ ), whereas the smallest O atom displacement magnitude, this time is for the O atom in the BaTiO<sub>3</sub> perovskite, only (-0.71% of  $a_0$ ) (Table 4). Finally, the third nearest neighbor A atom displacement directions and magnitudes are quite different (Table 4). The A atoms are attracted towards the PbZrO<sub>3</sub> and BaTiO<sub>3</sub> bulk *F*-center, whereas they are repulsed from the bulk *F*-center in the SrZrO<sub>3</sub> and SrTiO<sub>3</sub> matrixes (Table 4).

As we can see from Table 5, in most cases, the displacement magnitudes of three nearest neighbor atoms around the (001) surface *F*-center in ABO<sub>3</sub> perovskites are considerably larger than it was for the bulk *F*-center case (Table 4). For example, in the SrZrO<sub>3</sub> perovskite, the repulsion magnitudes of the Zr atoms from the (001) surface *F*-center (+9.17% of  $a_0$ ) is 2.49 times larger than for the bulk *F*-center case (+3.68% of  $a_0$ ) (Tables 4 and 5). Also, attraction magnitude of the O atom as well as repulsion magnitude of the Sr atom around the SrZrO<sub>3</sub> (001) surface center are 1.58 and 16.7 times larger, respectively, than around the SrZrO<sub>3</sub> bulk *F*-center (Tables 4 and 5). The single exception from this systematic trend is Ti atom repulsion from the BaTiO<sub>3</sub> (001) surface *F*-center, only (+0.1% of  $a_0$ ) (Table 5), which is smaller, than the Ti atom repulsion from the *F*-center located in the BaTiO<sub>3</sub> perovskite bulk (+1.06% of  $a_0$ ) (Table 4).

As we can see from Table 6, our *ab initio* B3PW computed charge inside the bulk *F*-center in SrZrO<sub>3</sub>, PbZrO<sub>3</sub> and BaTiO<sub>3</sub> perovskites always are larger than inside the (001) surface *F*-center (Table 6). The largest charge difference is between the PbZrO<sub>3</sub> bulk *F*-center charge (-0.68 $e$ ) and PbZrO<sub>3</sub> (001) surface *F*-center charge (-0.3 $e$ ) equal to 0.38 $e$ . Just opposite, the smallest charge difference is between the

Table 5. Our *ab initio* B3PW computed three nearest neighbor atom displacements around the (001) surface *F*-center located in the SZO, PZO, BTO and STO (% of  $a_0$ ).

Material	SZO	PZO	BTO	STO
B atom displ.	+9.17	+8.46	+0.1	+14.0
O atom displ.	-4.16	—	-1.4	-8.0
A atom displ.	+7.68	+11.97	+1.0	—

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Table 6. Our *ab initio* B3PW computed charge inside the SZO, PZO, BTO and STO bulk and (001) surface  $F$ -center (in  $e$ ).

Material	SZO	PZO	BTO	STO
Bulk $F$ -center charge	-1.25	-0.68	-1.103	-1.10
$F$ -center charge on (001) surface	-1.10	-0.3	-1.052	—
O atom net charge	-2.0	-2.0	-2.0	-2.0

BaTiO<sub>3</sub> bulk  $F$ -center charge ( $-1.103e$ ) and BaTiO<sub>3</sub> (001) surface  $F$ -center charge ( $-1.052e$ ) equal to only  $0.051e$  (Table 6). As we can see from Table 7, approximately 80%, 85% and 75% of charge are localized inside the BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk  $F$ -center, respectively. According to our performed *ab initio* B3PW computations, inside the  $F$ -center located on the BaF<sub>2</sub> (111) surface is localized slightly less charge, only  $-0.79e$ .

As we can see from Table 8 and Fig. 6, our *ab initio* B3PW computed direct bandgap values for SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbZrO<sub>3</sub> perovskites, containing the  $F$ -center defect, are equal to 5.07, 3.58, 3.63 and 3.97 eV, respectively. Our *ab initio* B3PW computed  $\Gamma$ - $\Gamma$  bandgap values for BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides, containing the  $F$ -center, are equal to 11.28, 11.34 and 10.99 eV, respectively. It is worth to note that the  $F$ -center induced defect level in the SrZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> perovskite bulk are located closer to the conduction band bottom, than to the valence band top. Namely, the  $F$ -center induced defect levels in SrZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> perovskite bulk are located 1.12, 0.23 and 0.69 eV below the CB bottom (Table 8 and Fig. 6). It is worth to note that the (001) surface  $F$ -center induced defect levels in the SrZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> perovskites, are located even closer to the CB bottom, than it was in the bulk case. Namely, the (001) surface  $F$ -center induced defect levels in SrZrO<sub>3</sub>, BaTiO<sub>3</sub> and SrTiO<sub>3</sub> perovskites are located only 0.93, 0.07 and 0.25 eV,

Table 7. Our *ab initio* B3PW computed charge inside the BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and (111) surface  $F$ -center (in  $e$ ).

Material	BaF <sub>2</sub>	SrF <sub>2</sub>	CaF <sub>2</sub>
Bulk $F$ -center charge	-0.801	-0.848	-0.752
$F$ -center charge on (111) surface	-0.790	—	—
F atom net charge	-1.0	-1.0	-1.0

Table 8. Our *ab initio* B3PW computed direct bulk bandgap for  $F$ -center containing BaF<sub>2</sub>, SrF<sub>2</sub>, CaF<sub>2</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbZrO<sub>3</sub> crystals as well as the  $F$ -center defect level induced position under the CB bottom (in eV).

Material	BaF <sub>2</sub>	SrF <sub>2</sub>	CaF <sub>2</sub>	SrZrO <sub>3</sub>	BaTiO <sub>3</sub>	SrTiO <sub>3</sub>	PbZrO <sub>3</sub>
Bulk bandgap with $F$ -center	11.28	11.34	10.99	5.07	3.58	3.63	3.97
Bulk $F$ -center under CB	4.27	3.67	4.24	1.12	0.23	0.69	1.72
Surface $F$ -center under CB	—	—	—	0.93	0.07	0.25	2.58

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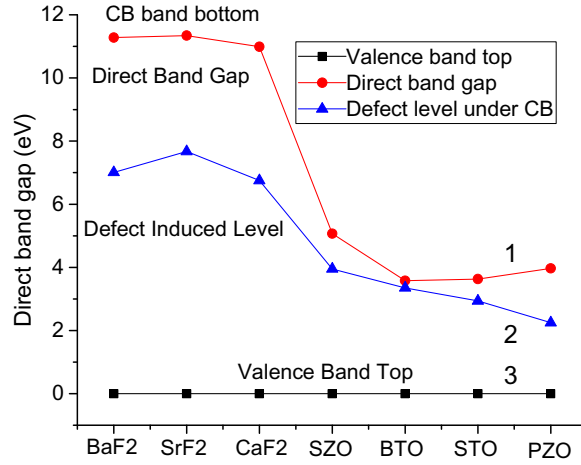


Fig. 6. (Color online) Our *ab initio* B3PW computed BaF<sub>2</sub>, SrF<sub>2</sub>, CaF<sub>2</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbZrO<sub>3</sub> direct bulk bandgap values for crystal containing the *F*-center (1) (in eV). The *F*-center induced defect levels inside the bandgap (2) as well as the VB top (3).

respectively, below the CB bottom (Table 8). The single exception from this systematic trend is PbZrO<sub>3</sub> perovskite, where the situation is just opposite. Namely, in the PbZrO<sub>3</sub> perovskite, the bulk *F*-center induced defect level is located 1.72 eV below the CB bottom, whereas the (001) surface *F*-center induced defect level is located 2.58 eV below the CB bottom (Table 8). In the BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluoride bulk, the *F*-center induced defect level, is located 4.27, 3.67 and 4.24 eV, respectively, below the CB bottom (Table 8 and Fig. 6). Based on our *ab initio* B3PW computed defect levels in the BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides, we proposed the theoretical mechanism for explanation of the optical absorption experiment data in this three fluoride crystals.<sup>76</sup> Namely, we suggest that the experimentally observed optical absorption energy in BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides (2.3, 2.85, 3.3 eV, respectively) may be explained via the electron transfer from the *F*-center ground state, located (4.27, 3.67 and 4.24 eV, respectively) below the CB bottom, to the conduction band (Table 8 and Fig. 6). As we can see from Table 9 and Fig. 7, our *ab initio* B3PW computed BaF<sub>2</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbZrO<sub>3</sub> bulk *F*-center formation energies are equal to 7.82, 7.55, 10.3, 7.1 and 7.25 eV, respectively. In contrast, our *ab initio* computed surface *F*-center formation energies always are smaller (Table 9).

Table 9. Our *ab initio* B3PW computed *F*-center formation energies in BaF<sub>2</sub> bulk and on its (111) surface as well as in SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbZrO<sub>3</sub> perovskite bulk and on their (001) surfaces (in eV).

Material	BaF <sub>2</sub>	SrZrO <sub>3</sub>	BaTiO <sub>3</sub>	SrTiO <sub>3</sub>	PbZrO <sub>3</sub>
Material bulk	7.82	7.55	10.3	7.1	7.25
Surface	7.48	7.52	10.2	6.22	6.0

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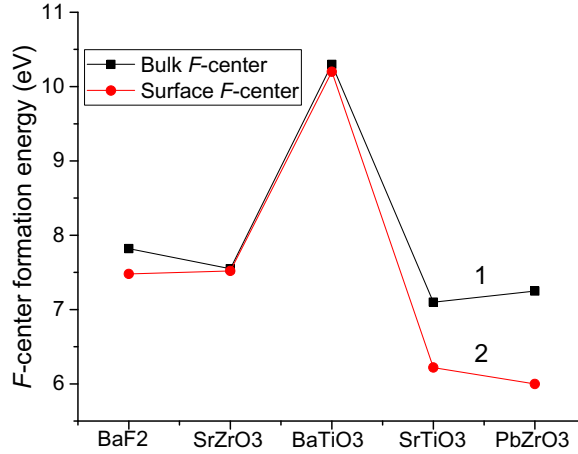


Fig. 7. (Color online) Our *ab initio* B3PW computed BaF<sub>2</sub>, SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbZrO<sub>3</sub> bulk (1) and surface (2) *F*-center formation energies (eV).

Namely, our *ab initio* B3PW computed *F*-center formation energy on BaF<sub>2</sub> (111) surface is equal to 7.48 eV, or by 0.34 eV smaller than it was in the BaF<sub>2</sub> bulk. Also, for SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbZrO<sub>3</sub> perovskites, our *ab initio* B3PW computed (001) surface energy (7.52, 10.2, 6.22 and 6.0 eV, respectively) is by (0.03, 0.1, 0.88 and 1.25 eV, respectively) smaller than it was in the bulk case (Table 9 and Fig. 7).

#### 4. Conclusion

The displacement magnitudes of atoms, surrounding the (001) surface *F*-center in SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbZrO<sub>3</sub> perovskites, in most cases, are considerably larger than the respective displacement magnitudes of atoms surrounding the bulk *F*-center. As a rule, the B atoms in ABO<sub>3</sub> perovskites are repulsed from the bulk and (001) surface *F*-center, whereas the O atoms are attracted towards the *F*-center. The atomic displacement magnitudes of atoms around the *F*-center in ABO<sub>3</sub> perovskites are much larger, than the respective atomic displacement magnitudes around the *F*-center in BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides.

The *F*-center formation energy, located on the (001) surface of ABO<sub>3</sub> perovskites as well as the (111) surface of BaF<sub>2</sub>, as a rule, is smaller than for the respective bulk *F*-centers. This slight energy distinction encourages the *F*-center segregation from the bulk of the ABO<sub>3</sub> perovskite and BaF<sub>2</sub> matrixes towards their (001) or (111) surfaces, respectively. In SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbZrO<sub>3</sub> perovskites as well as BaF<sub>2</sub>, the electron charge is better localized inside the bulk than the surface *F*-center. The charge inside the *F*-center is much better localized for BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides than SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub> and PbTiO<sub>3</sub> perovskites.

Our *ab initio* B3PW computed direct bandgaps in pristine SrZrO<sub>3</sub>, BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbZrO<sub>3</sub> perovskites as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides are in a fair

*ABO<sub>3</sub> perovskite as well as BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> bulk and surface F-center*


agreement with the available experimental data. In most cases, the introduction of the *F*-center defect, slightly increase their direct bandgap value. The ABO<sub>3</sub> complex oxide material (001) surface *F*-center generated defect levels, in most cases, are positioned nearer to the (001) surface conduction band (CB) bottom than the bulk *F*-center generated respective defect levels. We suggest that the experimentally observed optical absorption energy in BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub> fluorides (2.3, 2.85, 3.3 eV, respectively) may be explained via the electron transfer from the *F*-center ground state, located at (4.27, 3.67 and 4.24 eV, respectively) below the CB bottom, to the conduction band.

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### ORCID


Roberts Eglitis  <https://orcid.org/0000-0002-8772-257X>

J. Purans  <https://orcid.org/0000-0002-0358-6479>

A. I. Popov  <https://orcid.org/0000-0003-2795-9361>

S. Piskunov  <https://orcid.org/0000-0002-8768-0736>

Ran Jia  <https://orcid.org/0000-0002-3722-1195>

S. P. Kruchinin  <https://orcid.org/0000-0002-0674-5826>

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