

## *Ab initio* calculations of ABO<sub>3</sub> perovskite (001), (011) and (111) nano-surfaces, interfaces and defects

R. Eglitis\*

*Institute of Solid State Physics, University of Latvia,  
8 Kegaraga Street, Riga LV1063, Latvia  
rieglitis@gmail.com*

S. P. Kruchinin

*Bogolyubov Institute for Theoretical Physics, NASU,  
14-B, Metrolohichna Street, A-03143 Kyiv, Ukraine  
sergeikruchinin@yahoo.com*

Received 7 February 2020

Accepted 20 March 2020

Published 6 July 2020

We carried out *ab initio* calculations for technologically important ABO<sub>3</sub> perovskite, such as, SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (001), (011) and (111) nano-surfaces, interfaces and bulk *F*-centers. For SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (001) nano-surfaces, as a rule, all first surface layer atoms relax inward, whereas all second layer atoms relax outward, and, typically, all third surface layer atoms, again, relax inward. Calculated (001) surface energies for SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites are almost equal for both BO<sub>2</sub> and AO-terminations, and always smaller than the (011) and (111) surface energies. We discussed the results of our *ab initio* calculations dealing with BaTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) interfaces. We analyzed systematic trends in ABO<sub>3</sub> perovskite bulk *F*-center *ab initio* calculations.

*Keywords:* *Ab initio* calculations; ABO<sub>3</sub> perovskites; (001) surfaces; *F*-centers.

PACS Number(s): 71.15.Ap; 71.15.Mb; 71.20.-b; 71.55.-i

### 1. Introduction

Surface as well as interface phenomena, happening in the SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites and their nanostructures, the very complicated nature of their surface and interface states are extremely important topics in solid state physics.<sup>1–10</sup> SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> crystals all are the members of the so-called group of ABO<sub>3</sub> perovskites. ABO<sub>3</sub> perovskites have a large amount of technologically important applications as capacitors, actuators, water split implementations, as well as many others.<sup>11</sup> For all this applications, the ABO<sub>3</sub> perovskite

\*Corresponding author.

surface structure and quality are essential. Due to this technological importance, the ABO<sub>3</sub> perovskite neutral (001) surfaces were worldwide extensively explored both theoretically and experimentally.<sup>12–23</sup> It is much more difficult, at the *ab initio* level, to calculate the ABO<sub>3</sub> perovskite polar and charged as well as very complex (011)<sup>12–14,22,24–28</sup> and (111) surfaces.<sup>29–33</sup>

As an extension of our SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite neutral (001) as well as charged, polar and thereby very complex (011) and (111) surface studies, we performed *ab initio* calculations for the BaTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) interfaces. Taking into account the huge technological importance of ABO<sub>3</sub> perovskites and a large amount of *ab initio* studies dealing with their (001) surfaces, it is not clear, why only a very limited amount of theoretical and experimental studies exist dealing with their (001) heterostructures.<sup>34–38</sup>

It is well known that all physical properties of the complex oxide materials, like ABO<sub>3</sub> perovskites, are strongly affected by the point defects, such as the oxygen vacancies. Oxygen vacancy, or so-called neutral *F*-center, traps two electrons inside the vacancy in the ABO<sub>3</sub> perovskites. *Ab initio* calculations as well as experimental investigation of the *F*-centers in ABO<sub>3</sub> perovskites is a hot topic, since the *F*-center is the most common point defect, which strongly influence all material physical properties.<sup>39–44</sup>

## 2. Calculation Method

We carried out *ab initio* calculations for ABO<sub>3</sub> perovskite (001), (011), and (111) surfaces as well as their (001) heterostructures and *F*-centers therein by means of the hybrid exchange-correlation functionals B3LYP<sup>45</sup> or B3PW<sup>46</sup> as it is implemented in the world-famous CRYSTAL computer code.<sup>47</sup> The strong side of the CRYSTAL computer package is its ability to perform first principles calculations for two-dimensional isolated slabs perpendicular to the ABO<sub>3</sub> perovskite surface, without artificial periodicity in the *z* direction.

As an example, for calculations of ABO<sub>3</sub> perovskite (001) surfaces, we employed symmetrical slabs consisting of nine alternating neutral AO and BO<sub>2</sub>-terminated layers. First slab, in our calculations, was terminated from both sides by AO planes and consisted of a supercell containing 22 atoms. Our calculated second slab was terminated from both sides by BO<sub>2</sub>-planes, and, consequently, consisted from a supercell containing 23 atoms (Fig. 1). Both our calculated AO and BO<sub>2</sub>-terminated ABO<sub>3</sub> perovskite (001) slabs were non-stoichiometric, with unit cell equations A<sub>5</sub>B<sub>4</sub>O<sub>13</sub> and A<sub>4</sub>B<sub>5</sub>O<sub>14</sub>, respectively. Details of our calculations for very complex polar and charged ABO<sub>3</sub> perovskite (011) and (111) surfaces are described by us previously.<sup>12–14,30,32</sup>

By means of the same computer code CRYSTAL, we performed also the modelling of the SrZrO<sub>3</sub>/PbZrO<sub>3</sub> and BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) interfaces. For example, the calculations of the SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) interface were performed using the symmetrically terminated slab model. The SrZrO<sub>3</sub> substrate, in our calculations,

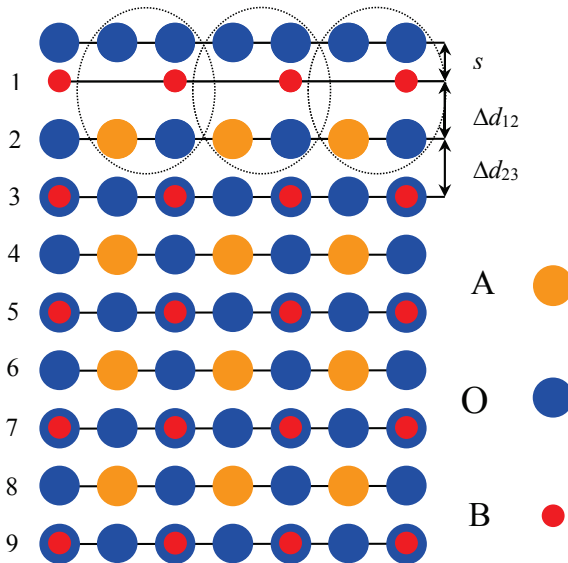


Fig. 1. (Color online) Side view of the BO<sub>2</sub>-terminated ABO<sub>3</sub> perovskite (001) surface.

contained 11 atomic layers and it was terminated from both sides by the ZrO<sub>2</sub> layer. As a next step, layer by layer epitaxial growth was modelled by adding a pair of PbZrO<sub>3</sub> layers symmetrically to the both sides of the SrZrO<sub>3</sub> substrate.

Lastly, the ABO<sub>3</sub> perovskite bulk *F*-center calculations were performed using the 3 × 3 × 3 times extended supercell. Such supercell in performed calculations contained 134 atoms as well as one isolated *F*-center. The *F*-center formation energy in the ABO<sub>3</sub> perovskites was calculated by means of the following equation:

$$E_{\text{form}}^{(F)} = E(\text{oxygen}) + E(F) - E(\text{perfect}), \quad (1)$$

where  $E_{\text{form}}^{(F)}$  is the *F*-center formation energy in the ABO<sub>3</sub> perovskite bulk.  $E(\text{oxygen})$  is our calculated total energy for the single oxygen atom. The  $E(\text{perfect})$  and  $E(F)$  are the calculated total energies for the pristine ABO<sub>3</sub> perovskite bulk, and the related ABO<sub>3</sub> perovskite bulk containing the single *F*-center defect.

### 3. *Ab Initio* Calculation Results

#### 3.1. Calculations for SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (001), (011) and (111) nano-surfaces

In order to start our calculations, we calculated the bulk lattice constants for SrTiO<sub>3</sub> (3.914 Å) and BaTiO<sub>3</sub> (4.021 Å) perovskites by means of the B3PW exchange-correlation functional and for SrZrO<sub>3</sub> (4.195 Å) and PbZrO<sub>3</sub> (4.220 Å) perovskites using the B3LYP exchange-correlation functional. We used our calculated cubic ABO<sub>3</sub> perovskite bulk lattice constants in all our performed calculations.

Table 1. Our calculated atomic relaxations (in percents of the bulk lattice constant) for the SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite AO and BO<sub>2</sub>-terminated (001) surfaces.

Material		SrTiO <sub>3</sub>	BaTiO <sub>3</sub>	SrZrO <sub>3</sub>	PbZrO <sub>3</sub>
(001)-terminat.		SrO	BaO	SrO	PbO
Layer	Ion	B3PW	B3PW	B3LYP	B3LYP
1	A	-4.84	-1.99	-7.63	-5.69
	O	0.84	-0.63	-0.86	-2.37
2	B	1.75	1.74	0.86	0.57
	O	0.77	1.40	-0.05	0.09
3	A	-	-	-1.53	-0.47
	O	-	-	-0.45	-0.47
(001)-terminat.		TiO <sub>2</sub>	TiO <sub>2</sub>	ZrO <sub>2</sub>	ZrO <sub>2</sub>
1	B	-2.25	-3.08	-1.38	-2.37
	O	-0.13	-0.35	-2.10	-1.99
2	A	3.55	2.51	2.81	4.36
	O	0.57	0.38	0.91	1.04
3	B	-	-	-0.04	-0.47
	O	-	-	-0.05	-0.28

As a next point of our calculations, we performed upper two or three layer atom relaxations for the neutral AO and BO<sub>2</sub>-terminated SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite (001) surfaces (Table 1). Systematic trend for the above mentioned four ABO<sub>3</sub> perovskites is that all upper layer atoms, with the single exception of the SrO-terminated SrTiO<sub>3</sub> (001) surface first layer O atom, relax inwards. At the same time, all second layer atoms, with an exception of the second layer SrO-terminated SrZrO<sub>3</sub> (001) O atom, relax outwards. Again, completely all third layer atoms, relax inwards. It is worth to notice, that all first layer metal and oxygen atom relaxation magnitudes are considerably larger than the respective third layer metal and also oxygen atom relaxation magnitudes (Table 1).

The atomic relaxation for different terminations of SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (011) surfaces are collected in Table 2. On the BO-terminated SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (011) surface B atoms move inward by 7.69, 7.86, 6.16 and 6.87% of  $a_0$ , respectively. Just opposite, first layer O atoms move outward by 3.59, 2.61, 4.36 and 4.27% of  $a_0$ , respectively (see Table 2), which leads to a large BO-terminated (011) surface rumpling. On the A-terminated SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (011) surfaces, the upper layer Sr, Ba, Sr and Pb atoms move extremely strongly inwards by 12.81, 8.67, 15.73 and 15.17% of  $a_0$ , respectively (Table 2). These our calculated upper layer Sr, Ba, Sr and Pb atomic displacements are the largest between all our calculated SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (011) surface atoms.

Table 2. Atomic relaxation of the SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (011) surface for the three terminations (in percent of the bulk lattice constant).

SrTiO <sub>3</sub> (011) surface				BaTiO <sub>3</sub> (011)		SrZrO <sub>3</sub> (011)		PbZrO <sub>3</sub> (001)	
Layer	Ion	$\Delta z$	$\Delta y$	$\Delta z$	$\Delta y$	$\Delta z$	$\Delta y$	$\Delta z$	$\Delta y$
TiO-terminated (011) surface				TiO-termin.		ZrO-termin.		ZrO-termin.	
1	B	-7.69	-	-7.86	-	-6.16	-	-6.87	-
	O	3.59	-	2.61	-	4.36	-	4.27	-
2	O	-0.51	-	-1.02	-	-0.38	-	-0.24	-
	A	-2.10	-	-0.88	-	-1.94	-	-2.37	-
3	O	-2.56	-	-	-	-5.69	-	-5.69	-
	B	0.16	-	-	-	0.40	-	-0.02	-
Sr-terminated (011) surface				Ba-termin.		Sr-termin.		Pb-termin.	
1	A	-12.81	-	-8.67	-	-15.73	-	-15.17	-
2	O	1.02	-	0.80	-	1.24	-	-0.57	-
	B	-0.04	-	0.16	-	0.10	-	-0.66	-
3	O	-1.08	-	-0.43	-	-0.95	-	2.37	-
	A	0.26	-	-	-	-0.48	-	3.41	-
O-terminated (011) surface				O-termin.		O-termin.		O-termin.	
1	O	-6.61	-0.14	-5.40	-1.67	-6.56	-3.58	-6.61	-3.55
	B	-1.02	-4.35	-0.15	-6.38	1.45	-4.29	0.73	-4.53
2	A	-1.18	0.85	1.54	-1.27	-1.43	-0.24	0.73	-3.79
	O	1.79	6.40	1.95	2.97	4.29	7.87	4.29	7.94
3	O	-0.79	2.10	0.90	4.49	-0.10	1.74	-0.19	1.66

Table 3. *Ab initio* calculated surface energies (in eV per surface cell) for SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> (001), (011) and (111) surfaces.

Material	SrTiO <sub>3</sub>	BaTiO <sub>3</sub>	SrZrO <sub>3</sub>	PbZrO <sub>3</sub>
Termination	<i>Ab initio</i> calculated surface energies for (001) surfaces			
AO	1.15	1.19	1.13	1.00
BO <sub>2</sub>	1.23	1.07	1.24	0.93
	<i>Ab initio</i> calculated surface energies for (011) surfaces			
BO	3.06	2.04	3.61	1.89
A	2.66	3.24	2.21	1.74
O	2.04	1.72	2.23	1.85
	<i>Ab initio</i> calculated surface energies for (111) surfaces			
AO <sub>3</sub>	6.30	8.40	9.45	8.21
B	4.99	7.28	7.98	6.93

As it is possible to see from Table 3, our at *ab initio* level calculated SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> neutral (001) surface energies for both BO<sub>2</sub> and AO-terminations are almost equal for all calculated perovskites, whereas polar (011) and (111) surface energies are completely different for different terminations. It is important, that the (111) polar surface energies, for both terminations, are always larger than the polar (011) surface energies. At the same time, polar (011) surface energies, again, for all terminations, always are larger than the neutral (001) surface energies.

### 3.2. *Ab initio calculations of BaTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) interfaces*

We carried out first principles calculations dealing with BaTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) heterostructures.<sup>35,38</sup> As an example we will analyze the BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) heterostructure. For our calculations, we used as a substrate 11 layer thick symmetrical SrTiO<sub>3</sub> (001) slab from both sides terminated by TiO<sub>2</sub> (001) layers. As a next step, we augmented to both sides of this SrTiO<sub>3</sub> (001) substrate one layer of BaO-terminated BaTiO<sub>3</sub> (001) slab. As a result, our calculated band gap of this 13-layer containing BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) interface is equal to 3.47 eV. In case, when we add to the SrTiO<sub>3</sub> (001) substrate from both sides 3, 5, 7, 9 BaO-terminated BaTiO<sub>3</sub> layers, the band gap of our calculated BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) interface is equal to 3.29, 3.25, 3.24 and 3.22 eV. So, it means, that the BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) heterostructure band gap slowly decrease with the number of augmented layers from 3.47 eV (1 augmented BaO-terminated layer from both sides) till 3.22 eV (for the case when there are 9 augmented BaO-terminated BaTiO<sub>3</sub> layers from the both sides of the SrTiO<sub>3</sub> substrate). In case, when we augment on the SrTiO<sub>3</sub> substrate from both sides 2, 4, 6, 8 and 10 TiO<sub>2</sub>-terminated BaTiO<sub>3</sub> (001) layers, the BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) interface band gap is equal to 2.33, 2.16, 2.10, 2.06, 2.06 eV, respectively.

### 3.3. *Ab initio calculations of BaTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) interfaces*

By means of the hybrid exchange-correlation functional B3PW calculated nearest atom displacements surrounding the *F*-center in the SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites are summarized in Table 3 as well as compared with related results obtained for another ABO<sub>3</sub> perovskites.

As it is possible to see from Table 4, the two nearest neighbors to the *F*-center in the BaTiO<sub>3</sub> perovskite Ti atoms are repulsed by 1.06% of  $a_0$  from the oxygen vacancy. Also in the SrTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> crystals, the B atoms are repulsed from the oxygen vacancy by 7.76, 3.68 and 0.48% of the bulk lattice constant  $a_0$ . Just opposite, the second nearest neighbor O atoms in the SrTiO<sub>3</sub>, BaTiO<sub>3</sub> and SrZrO<sub>3</sub> materials, as a rule, are attracted towards the oxygen vacancy by 7.79, 0.71 and 2.63% of the  $a_0$ .

Table 4. *Ab initio* calculated main characteristics of bulk *F*-center in SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites.

Bulk <i>F</i> -center characteristics	SrTiO <sub>3</sub>	BaTiO <sub>3</sub>	SrZrO <sub>3</sub>	PbZrO <sub>3</sub>
<i>F</i> -center charge (in <i>e</i> )	-1.1	-1.103	-1.25	-0.68
<i>F</i> -center level under CB (eV)	0.69	0.23	1.12	1.72
<i>F</i> -center formation energy (eV)	7.1	10.3	7.55	7.25
B atom relaxation (% of <i>a</i> <sub>0</sub> )	7.76	1.06	3.68	0.48
O atom relaxation (% of <i>a</i> <sub>0</sub> )	-7.79	-0.71	-2.63	-
A atom relaxation (% of <i>a</i> <sub>0</sub> )	3.94	-0.08	0.46	-5.99

Inside the oxygen vacancy in SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites are located -1.1, -1.103, -1.25 and -0.68 electrons of the additional charge. The *F*-center formation energy for SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites are in the range between 7.1 and 10.3 eV. The *F*-center defect induced levels are located 0.69, 0.23, 1.12 and 1.72 eV below the conduction band bottom in the SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites.

#### 4. Conclusions

SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite neutral (001) surface upper layer atoms, with a very few exceptions, relax inwards, the second layer atoms relax outwards, and again, third layer atoms relax inwards. The SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite (001) surface energies for both possible BO<sub>2</sub> and AO terminations are almost equal. The SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite polar (111) surface energies are considerably larger than the polar (011) surface energies. The neutral SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskite (001) surface energies are always smaller than the polar (011) and especially polar (111) surface energies. The BaTiO<sub>3</sub>/SrTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) interface band gaps depend much more strongly from the termination of the upper interface layer (BO<sub>2</sub> or AO) than from the number of augmented layers. The results of calculations for the bulk *F*-centers in SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites are presented, and systematic trends, common for the *F*-center defects in SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, SrZrO<sub>3</sub> and PbZrO<sub>3</sub> perovskites are analyzed.

#### Acknowledgements

S. P. Kruchinin acknowledges support by the National Academy of Sciences of Ukraine project “Functional properties of materials prospective for nanotechnologies” (No. 0120U100858).

#### References

1. M. Dawber, K. M. Rabe and J. F. Scott, *Rev. Mod. Phys.* **77** (2005) 1083.
2. M. M. Kuklja, E. A. Kotomin, R. Merkle, Y. A. Mastrikov and J. Maier, *Phys. Chem. Chem. Phys.* **15** (2013) 5443.

3. R. A. P. Ribeiro, J. Andrés, E. Longo and S. R. Lazaro, *Appl. Surf. Sci.* **452** (2018) 463.
4. S. Gerhold, Z. Wang, W. G. Schmidt and U. Diebold, *Surf. Sci.* **621** (2014) L1.
5. G. R. Portugal, S. F. Santos and J. T. Arantes, *Appl. Surf. Sci.* **502** (2020) 144206.
6. Y. Wei, Y. Y. Sun, J. Yang, S. J. Gong, Y. H. Meng and C. G. Duan, *J. Phys.: Condens. Matter* **31** (2019) 075803.
7. V. S. Vikhnin, H. M. Liu, W. Y. Jia, S. E. Kapphan, R. Eglitis and D. Usvyat, *J. Luminescence* **83–84** (1999) 109.
8. S. P. Repetsky, I. G. Vyshyvana, S. P. Kruchinin and S. Bellucci, *Sci. Rep.* **8** (2018) 9123.
9. S. P. Kruchinin, A. Zolotovskiy and H. T. Kim, *J. Mod. Phys.* **4** (2013) 608.
10. S. P. Repetsky, I. G. Vyshyvana, E. Ya. Kuznetsova and S. P. Kruchinin, *Int. J. Mod. Phys. B* **32** (2018) 1840030.
11. H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa and Y. Tokura, *Nat. Mater.* **11** (2012) 103.
12. R. I. Eglitis and D. Vanderbilt, *Phys. Rev. B* **78** (2008) 155420.
13. R. I. Eglitis and D. Vanderbilt, *Phys. Rev. B* **76** (2007) 155439.
14. R. I. Eglitis and D. Vanderbilt, *Phys. Rev. B* **77** (2008) 195408.
15. Y. Lin, A. E. Becerra-Toledo, F. Silly, K. R. Poepelmeier, M. R. Castell and L. D. Marks, *Surf. Sci.* **605** (2011) L51.
16. M. Saghayezhian, S. M. R. Sani, J. D. Zhang and E. W. Plummer, *J. Phys. Chem. C* **123** (2019) 8086.
17. E. Heifets, R. I. Eglitis, E. A. Kotomin, J. Maier and G. Borstel, *Phys. Rev. B* **64** (2001) 235417.
18. M. G. Brik, C. G. Ma and V. Krasnenko, *Surf. Sci.* **608** (2013) 146.
19. G. Borstel, R. I. Eglitis, E. A. Kotomin and E. Heifets, *Phys. Status Solidi B* **236** (2003) 253.
20. B. Luo, X. Wang, E. Tian, G. Li and L. Li, *Appl. Surf. Sci.* **351** (2015) 558.
21. E. A. Kotomin, R. I. Eglitis, J. Maier and E. Heifets, *Thin Solid Films* **400** (2001) 76.
22. R. I. Eglitis and M. Rohlfing, *J. Phys.: Condens. Matter* **22** (2010) 415901.
23. J. R. Sambrano, V. M. Longo, E. Longo and C. A. Taft, *J. Mol. Struct.: THEOCHEM* **813** (2007) 49.
24. R. I. Eglitis, *Ferroelectrics* **483** (2015) 53.
25. R. I. Eglitis, J. Kleperis, J. Purans, A. I. Popov and R. Jia, *J. Mater. Sci.* **55** (2020) 203.
26. J. Wang, G. Tang and X. S. Wu, *Phys. Status Solidi B* **249** (2012) 796.
27. Y. Xie, H. T. Yu, G. X. Zhang, H. G. Fu and J. Z. Sun, *J. Phys. Chem. C* **111** (2009) 6343.
28. H. Chen, Y. Xie, G. H. Zhang and H. T. Yu, *J. Phys.: Condens. Matter* **26** (2014) 395002.
29. N. Sivadas, H. Dixit, V. R. Cooper and D. Xiao, *Phys. Rev. B* **89** (2014) 075303.
30. R. I. Eglitis, *Solid State Ionics* **230** (2013) 43.
31. W. Liu, C. Wang, J. Cui and Z. Y. Man, *Solid State Commun.* **149** (2009) 1871.
32. R. I. Eglitis, *Appl. Surf. Sci.* **358** (2015) 556.
33. R. I. Eglitis, *Phys. Status Solidi B* **252** (2015) 635.
34. Z. Bi, B. P. Uberuaga, L. J. Vernon, E. Fu, Y. Wang, N. Li, H. Wang, A. Misra and Q. X. Jia, *J. Appl. Phys.* **113** (2013) 023513.
35. S. Piskunov and R. I. Eglitis, *Solid State Ionics* **274** (2015) 29.
36. V. Stepkova, P. Marton, N. Setter and J. Hlinka, *Phys. Rev. B* **89** (2014) 060101.



37. R. I. Eglitis, S. Piskunov and Y. F. Zhukovskii, *Phys. Status Solidi C* **13** (2016) 913.
38. S. Piskunov, R. I. Eglitis, *Nucl. Instrum. Methods B* **374** (2016) 20.
39. E. A. Kotomin, S. Piskunov, Y. F. Zhukovskii, R. I. Eglitis, A. Gopeyenko and D. Ellis, *Phys. Chem. Chem. Phys.* **10** (2008) 4258.
40. S. Piskunov, A. Gopeyenko, E. A. Kotomin, Y. F. Zhukovskii and D. Ellis, *Comput. Mater. Sci.* **41** (2007) 195.
41. R. I. Eglitis and S. Piskunov, *Comput. Condens. Matter* **7** (2016) 1.
42. Y. F. Zhukovskii, E. A. Kotomin, S. Piskunov and D. Ellis, *Solid State Commun.* **149** (2009) 1359.
43. J. Carrasco, F. Illas, N. Lopez, E. A. Kotomin, Y. F. Zhukovskii, R. A. Evarestov, Y. A. Mastrikov, S. Piskunov and J. Maier, *Phys. Rev. B* **73** (2006) 064106.
44. M. Sokolov, R. I. Eglitis, S. Piskunov and Y. F. Zhukovskii, *Int. J. Mod. Phys. B* **31** (2017) 1750251.
45. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **37** (1988) 785.
46. A. D. Becke, *J. Chem. Phys.* **98** (1993) 5648.
47. V. R. Saunders, R. Dovesi, C. Roetti, N. Causa, N. M. Harrison, R. Orland, C. M. Zicovich-Wilson, *CRYSTAL-2009 User Manual*, University of Torino, Italy (2009).