

Structural and Electronic Properties of PZT

Alfredo Sánchez*^{a,b}, César Zambrano^b, Luis Miguel Prócel^{a,b}, Arvids Stashans^{a,b}

^aCentro de Investigación en Física de la Materia Condensada, Corporación de Física Fundamental y Aplicada, Apartado 17-12-637, Quito Ecuador

^bDepartamento de Química, Colegio Politécnico, Universidad San Francisco de Quito, Apartado 17-12-841, Quito, Ecuador

ABSTRACT

The structural and electronic properties of Zr-doped PbTiO_3 crystals are investigated. A quantum-chemical INDO method based on the Hartree-Fock theory is employed, along with a periodic large unit cell (LUC) model, as implemented into the computational program SYM-SYM. The most stable defect configurations found to be those that allow the maximum displacements of oxygen atoms – and the atomic relaxation around the Zr impurity are described for different impurity concentrations. Results are compared with those from various theoretical and experimental studies.

Keywords: lead titanate, Zr doping, LUC, structural and electronic properties

1. INTRODUCTION

Perovskite-type titanates have attracted many researchers since the discovery of ferroelectricity in barium titanate in the late 1940s. Afterwards, several studies have revealed numerous interesting attributes of these materials. Among these, pure lead titanate (which has the chemical formula PbTiO_3) and Zr-doped lead titanates ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, also known as PZT ceramics) are seriously considered for many optical, memory, sensor and actuation applications due to their piezoelectric, dielectric and ferroelectric properties.

Perovskite-type titanates have a chemical formula ATiO_3 , where A can be a Ba, Sr, Ca or Pb cation. In the cubic perovskite structure having the space group $Pm\bar{3}m$, Ti atoms are at the cube centers, A atoms at the cube corners and O atoms at the face centers. At temperatures below 766 K lead titanate switches from cubic to tetragonal phase and exhibits ferroelectricity. Consequently, study of both phases is necessary for a better understanding of the aforementioned characteristics of these materials.

It is important to mention that PbTiO_3 and similar ferroelectric materials possess a nonvolatile, reversible polarization field, which has been effectively employed in radiation “hard” memories.¹ On the other hand, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ is suitable for ultrasonic and sonar listening appliances with improved resolution and range. PZT ceramics may be also employed in high-density storage media and integrated components for use in nonvolatile, dynamic random access memories. They also could be useful inside devices designed for surface acoustic wave, micromechanical, and ferroelectric field effect purposes.^{2,3}

Lead titanate has been studied so far using various theoretical methods.⁴⁻⁶ It has been found that the ferroelectricity is vastly determined by the covalent interaction between the Ti and O ions.^{7,8} Additionally, a lot of experiments has been performed on Zr-doped lead titanate.⁹⁻¹² Despite these investigations, a large portion of the properties of lead titanate (and titanates in general) has not been entirely explained at the quantum-chemical (fundamental) level, a fact that attracts the attention of the scientific community.

In a recent study by our group,¹³ the properties of pure PbTiO_3 have been analyzed extensively, and the structure of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ crystals for $x = 0.125$ and 0.25 (i.e. 12.5 and 25 percent of Ti atoms being replaced by Zr atoms) has been described. The purpose of the present work is to extend the study of the structural and electronic properties of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (for x up to 0.5), for both cubic and tetragonal lattices. The results obtained are discussed in terms of other available theoretical and experimental data.

2. DESCRIPTION OF THE COMPUTATIONAL METHOD

A periodic large unit cell (LUC) model¹⁴ is used throughout the study as it is implemented in the computational program SYM-SYM.¹⁵ It exploits a semi-empirical quantum-chemical INDO method based on the Hartree-Fock theory. The calculations are carried out using a non-relativistic valence basis set consisting of the following atomic orbitals (AOs): lead 5d, 6s and 6p AOs, titanium 3d, 4s and 4p AOs, zirconium 4d, 5s and 5p, and finally oxygen 2s and 2p AOs. Although the main computational equations and the fundamentals for the total energy calculations have been described extensively elsewhere,^{14,16} it is useful to point out the basic idea of the LUC formalism, the so-called $k = 0$ approximation. The self-consistency of the Fock matrix elements in this case is achieved by obtaining the density matrix elements in the following manner:

$$P_{pq}^0 = \frac{1}{N} \sum_k P_{pq}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{R}_v) \quad (1)$$

Here, the summation is carried out over all k values in the reduced Brillouin zone (BZ) of the LUC. The information obtained corresponds only to the point $k = 0$ of the density matrix, $P_{pq}(\mathbf{k})$. Nevertheless, it has been proven^{14,17} that this is equivalent to a band structure calculation at those k points, which transform to the reduced BZ center after the extension of the primitive unit cell. In this work, eight k points were included in the band structure calculations. This was achieved by using a 40-atom LUC, which corresponds to an eight-fold ($2 \times 2 \times 2$) extended primitive unit cell. Many recent studies¹⁸⁻²⁰ show that an eight-fold or even a four-fold symmetric extension of the primitive unit cell is sufficient to reproduce correctly the electronic band structure of a given crystal. One more point to mention is that the periodic LUC model is free from the limitations of different cluster models applicable mainly to materials with a wide band-gap, and also the LUC approach allows a precise calculation of impurity concentrations.

It can be mentioned that the SYM-SYM computer code contains a number of adjustable parameters. They simplify known two-center integrals in the intermediate neglect of differential overlap (INDO) approximation – hence its semi-empirical denomination. As a result, this method is more suitable than non-empirical ones in order to study complex systems, since it is more manageable and time-effective in the treatment of electronic and spatial structures of systems. The computer code predicts successfully the geometry for crystals doped with impurity atoms.^{21,22} Furthermore, since there are not any *a priori* assumptions regarding the pattern of the electronic density distribution around the defect under study, i.e. calculations are made through a self-consistent field (SCF) approach, the obtained results are very reliable. As an example of the reliability of the computer program, it can be mentioned the computation of the band-gap width for the TiO₂ crystal where the value obtained through a semi-empirical method²³ is closer to an experimental value than the one calculated with an *ab initio* method.²⁴

Because of the above-mentioned reasons, the aforesaid method has been successfully used to reproduce the spatial and electronic properties of a wide variety of pure and defective crystals. The list includes complex oxides such as α -Al₂O₃²⁵⁻²⁷, WO₃²⁸, MgO²⁹ and TiO₂^{19-21, 30}, and perovskite-type crystals such as KNbO₃^{31, 32}, Nb-doped KTaO₃³³, BaTiO₃³⁴⁻³⁷, SrTiO₃³⁸⁻⁴² and CaTiO₃⁴³⁻⁴⁴. Regarding the numerical parameters used in the present study we can say that they were obtained in our previous work.¹³

3. RESULTS AND DISCUSSION

3.1. Properties of PbZr_{0.125}Ti_{0.875}O₃

As stated above, a 40-atom LUC has been used to perform the calculations. In order to study the PbZr_{0.125}Ti_{0.875}O₃ ($x = 0.125$) structure, one Ti atom was substituted by a single Zr atom. The insertion of Zr is a perturbation of the otherwise perfect crystalline lattice; accordingly, atomic displacements are expected in order to stabilize the system and reduce its total energy. Changes in the electronic configuration are also anticipated.

3.1.1. Structural properties

Different kinds of atomic relaxation, including non-symmetric lattice distortion, were considered. As a result of performed computations two spatial configurations were found to be stable, one for each of the two crystallographic lattices.

It was found for the cubic structure that each of the six oxygen atoms closest to the impurity moved outwards by 0.19 Å. These displacements were along the $\langle 100 \rangle$ directions. In the case of the tetragonal structure, outward movements for both O and Pb atoms were observed. The O atoms moved away from the Zr impurity along the $\langle 100 \rangle$ directions. However, these movements were not completely symmetric in contrast to those found in the cubic phase, i.e. the displacements along the z -

axis were found to be shorter (0.16 Å) than those within the *xy*-plane (0.19 Å). Additionally, the eight Pb atoms surrounding the impurity experienced outward displacements by about 0.07 Å along the $\langle 111 \rangle$ directions.

The observed oxygen movements can be described in terms of Coulomb interaction. The Zr atom is less positive than the Ti atom it replaces. As it was found for the cubic phase, $q_{Zr} = 2.08 e$ and $q_{Ti} = 2.55 e$, while $q_{Zr} = 1.99 e$ and $q_{Ti} = 2.47 e$ for the tetragonal lattice. The charges on Ti atoms are averaged since they are slightly different depending on their relative positions with respect to the Zr impurity. In addition, the slightly shorter movements along the *z*-axis observed in the tetragonal phase could be due to the phenomenon of ferroelectricity occurring in this phase of the material. On the other hand, the larger size of the Zr atoms compared to the Ti ones, and the resulting larger repulsion between the overlapping electron clouds of Zr and surrounding Pb atoms can explain the Pb displacements that take place in the tetragonal phase.

3.1.2. Electronic properties

The optical band-gap was calculated using two methods. For the cubic phase, the band-gap obtained by the Δ SCF method was found to be equal to 6.01 eV, while the value obtained from the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) was about 8.16 eV. The corresponding values for the tetragonal phase were 5.29 eV (the Δ SCF method) and 7.91 eV (as the difference between the HOMO and the LUMO). The increased covalent bonding in the tetragonal phase is likely to cause the reduced band-gap width compared to that of the cubic lattice.

In the cubic lattice, the upper valence band (UVB) is conformed mainly by Pb 6s atomic orbitals with some contribution of O 2p AOs, at least until the one-electron energy is 1.2 eV below the HOMO. In the lower part of the UVB, about 4.3 eV below the HOMO, presence of O 2p AOs become evident with smaller contribution of Zr 4d, Ti 3p and Ti 3d states. Meanwhile, the bottom of the conduction band (CB) is made up of Pb 6p states and small contributions (~15%) of Zr 4d and Ti 3d AOs. For the tetragonal phase, the composition of the UVB and the CB is similar to that of the cubic phase, with the UVB having increased influence of Zr 4d and Ti-3d AOs. We also observe the 2p-3d hybridization between the oxygen and titanium orbitals. Pb 6p, Zr 4d and Ti 3d AOs constitute the conduction band, as in the cubic phase.

3.2. Properties of $PbZr_{0.25}Ti_{0.75}O_3$

3.2.1. Structural properties

$PbZr_{0.25}Ti_{0.75}O_3$ ($x = 0.25$) is obtained by replacing two of the eight Ti atoms with the Zr atoms in the LUC. Since the two impurities can be placed in diverse manners, we have considered their situation along the $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ directions for both cubic and tetragonal phases.

The atomic displacements are similar to those observed for $x = 0.125$. In the cubic phase, the twelve oxygen atoms that surround their Zr counterparts experience outward movements along the $\langle 100 \rangle$ directions by 0.19 Å. In the tetragonal lattice, outward O motion with respect to the impurities is found again. The asymmetry in oxygen atomic relaxation is observed again similar as for the lower impurity concentration discussed above: oxygen displacements within the *xy*-plane are larger (0.19 Å) than those along the *z*-axis (0.16 Å). Pb movements are absent for both lattices in the case of $x = 0.125$.

The explanation of these movements resembles those already discussed for the previous case ($x = 0.125$). The Coulomb interaction between Zr and O atoms is different compared to the interaction between Ti and O atoms, which originates from the different charges: $q_{Zr} = 2.06 e$ (cubic), 1.91 e (tetragonal), while $q_{Ti} = 2.49 e$ (cubic), 2.43 e (tetragonal). Additionally, the ferroelectricity of the tetragonal phase seems to have an important role in the asymmetry of the oxygen displacements along the *z*-axis.

3.2.2. Electronic properties

For the cubic lattice, the computed values for the optical band-gap width were found to be equal to 6.04 eV using the Δ SCF method and 7.03 eV as the difference between the HOMO and the LUMO. For the tetragonal phase, the corresponding energies were obtained to be 4.83 eV and 5.18 eV, respectively. It is obvious that the reason for the narrower band-gap in the tetragonal phase is the same as for $x = 0.125$.

The UVB in the cubic lattice is predominantly Pb 6s in nature until the one-electron energy diminishes to 1.3 eV below the HOMO level. Afterwards O 2p states appear to be prevalent with significant contribution of Zr 4d and somewhat of Ti 3d AOs. Pb 6p AOs with some admixture of Zr 4d and Ti 3d states mainly compose the bottom part of the CB. On the other hand, the UVB for the tetragonal structure also exhibits very significant contribution of Pb 6s states up to one-electron energies of 1.7 eV below the HOMO. From then on, O 2p AOs become predominant with a significant admixture of Zr 4d

AOs and smaller contribution of Ti 3d, Ti 4p, Pb 6p and Pb 5d states. The CB is formed mostly of Pb 6p states similarly as for the cubic phase.

3.3. Properties of $\text{PbZr}_{0.375}\text{Ti}_{0.625}\text{O}_3$

3.3.1. Structural properties

In this case three Zr atoms substitute for three of the eight Ti atoms in the LUC leading to a number of diverse configurations of the impurity location. After analyzing numerous different cases, the most stable configuration was obtained when the second Zr atom is situated along the $\langle 110 \rangle$ direction and the third one is along the $\langle 011 \rangle$ direction. Such a configuration was found to be the most stable for both cubic and tetragonal phases.

Similar to the previous cases the O atoms surrounding the Zr impurities move away from the impurities along the $\langle 100 \rangle$ directions. Movements are symmetric (0.19 Å) for the cubic phase and slightly asymmetric in the tetragonal structure maintaining the same tendency: they are smaller along the z -axis (0.16 Å) than within the xy -plane (0.19 Å). Pb atoms displacements are absent in the cubic phase, but are found to be an important feature in the tetragonal lattice. Four Pb atoms situated below the Zr impurities move along the $\langle 101 \rangle$ direction by 0.06 Å. The remaining atoms move along the $\langle 111 \rangle$ directions by 0.07 Å. Their displacements are such that they came closer to each other but farther from any of the impurities and approach slightly neighboring Ti atoms. The Zr atoms are significantly larger than Ti atoms and consequently exert a larger repulsion between the overlapping electron clouds (such as those between Zr and Pb) and thus explain the pattern observed.

3.3.2. Electronic properties

The values of the optical band-gap widths for the cubic structure are found to be equal to 4.62 eV (using the ΔSCF approach) and 6.31 eV (as the HOMO-LUMO difference). The upper valence band is formed by Pb 6s AOs and at lower one-electron energies, 5.4 eV below the HOMO, O 2p states acquire more relevance with some admixture of Zr 4d, Ti 3d and Ti 3p orbitals. The CB for this lattice is composed, similar to the previous cases, mainly by Pb 6p AOs with minor contribution of Zr 4d and Zr 5s states.

For the tetragonal lattice the corresponding values of the optical band-gap width were obtained to be 3.25 eV (the ΔSCF method) and 5.09 eV (as the HOMO-LUMO difference). The UVB, similar to the one of the cubic structure, consists of Pb 6s states at one-electron energies close to the UVB top and O 2p AOs as energy diminishes with additional contribution of Zr 4d, Ti 4s and Ti 3d AOs. The CB is constituted by Pb 6p (~50%) AOs with some admixture of Zr 5s, Zr 4d and O 2p AOs.

3.4. Properties of $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$

3.4.1. Structural properties

The substitution of four Ti atoms with Zr impurities leads to a Zr-doped lead titanate with $x = 0.5$. Among the different options available for the impurity placing, the optimum geometry for the system was obtained by putting two Zr impurities along the $\langle 110 \rangle$ direction and the other two along the $\langle 011 \rangle$ direction. Thus the impurities find themselves located in highly symmetric positions, actually they resemble a tetrahedron.

The obtained distribution of the Zr atoms within the LUC allows all the O atoms to have outward displacements from the impurity atoms along the $\langle 100 \rangle$ directions as described above for smaller impurity concentrations. The magnitudes of these movements are found to be 0.19 Å for both cubic and tetragonal phases except the motions along the z -axis in the tetragonal structure where shorter displacements of 0.16 Å were obtained. The obtained pattern of atomic displacements is consistent with a couple of facts. First, Zr atoms are bigger than Ti atoms and as a result the repulsion of overlapping electron clouds increases. Moreover, the interaction between Zr and O atoms is more covalent compared to the one between Ti and O atoms, so the distance that separates Zr and O atoms should increase accordingly. The ferroelectricity that exists in the tetragonal phase of the material can explain again the shorter displacements observed along the ferroelectric z -axis. At this point, it is important to state that similar non-symmetric atomic motion along the ferroelectric z -axis has been reported in studies of impurity doping in SrTiO_3 ³⁸ and BaTiO_3 crystals.^{35,37} Finally, it should be mentioned that in the tetragonal lattice Pb atoms move away from the closest impurity along the $\langle 111 \rangle$ directions, without closing on any of the remaining impurities. This implies that size difference between Zr and Ti is possibly the predominant factor for such a lattice distortion.

3.4.2. Electronic properties

The optical band-gap width values calculated using the Δ SCF method were obtained to be equal to 3.54 eV (cubic structure) and 4.87 eV (tetragonal structure). Taking the difference between the HOMO and LUMO magnitudes, the obtained band-gap width values were found to be 6.42 eV and 6.59 eV for cubic and tetragonal lattices, respectively. The UVB of the cubic structure is formed exclusively by Pb 6s states while O 2p and Zr 4d orbitals appear well below the HOMO (about 3.0 eV). The conduction band is made up of Pb 6p and Zr 4d AOs. The tetragonal structure has very similar composition of the UVB with Pb 6s states being the most significant, but it has also some contribution of O 2p and Ti 3d AOs. The CB consists of Pb 6p and Zr 4d states with less contribution from Ti 3d, Ti 4s and Zr 5s states.

3.5. Comparison between pure and Zr-doped PbTiO₃

According to our calculations, the covalent chemical bonding increases its importance as the impurity concentration increases. This was expected since the interaction between Zr and O atoms differs from the one between Ti and O atoms in sense they are more covalent. Additionally, the chemical bonding is more covalent in the tetragonal structure compared to the cubic one. This effect is seen from tables 1 and 2, where the variation in the atomic charges is given.

Table 1. Average atomic charges in pure and Zr-doped PbTiO₃, cubic lattice.

Atom type	Average atomic charges (<i>e</i>)				
	PbTiO ₃ (Ref. 13)	PbZr _{0.125} Ti _{0.875} O ₃	PbZr _{0.25} Ti _{0.75} O ₃	PbZr _{0.375} Ti _{0.625} O ₃	PbZr _{0.5} Ti _{0.5} O ₃
Pb	1.68	1.67	1.66	1.64	1.61
Ti	2.49	2.44	2.42	2.40	2.37
Zr	-	2.08	2.06	2.02	1.99
O	-1.39	-1.38	-1.37	-1.35	-1.31

Table 2. Average atomic charges in pure and Zr-doped PbTiO₃, tetragonal lattice.

Atom type	Average atomic charges (<i>e</i>)				
	PbTiO ₃	PbZr _{0.125} Ti _{0.875} O ₃	PbZr _{0.25} Ti _{0.75} O ₃	PbZr _{0.375} Ti _{0.625} O ₃	PbZr _{0.5} Ti _{0.5} O ₃
Pb	1.66	1.65	1.65	1.63	1.62
Ti	2.38	2.37	2.34	2.30	2.26
Zr	-	1.99	1.91	1.85	1.80
O	-1.36	-1.29	-1.27	-1.25	-1.24

4. CONCLUSIONS

The quantum-chemical INDO method developed for crystal studies has been used in the present work. The structural and electronic properties of PZT with different zirconium concentrations have been studied. The atomic displacements obtained around the Zr impurities indicate the importance of the electrostatic Coulomb interaction in these materials. However, in a number of cases one has to take into account also the effect of the repulsion between overlapping electron clouds. This effect is especially noticeable in the tetragonal phase, where the asymmetry along the ferroelectric *z*-axis should be taken into account in order to explain the displacements of O atoms. The study of electronic properties reveals some important differences between the pure PbTiO₃ crystal and the PZT materials. In particular, we notice the augmentation of Zr 4d states in the bottom of the CB increasing the impurity concentration. Since Zr atoms are less positive compared to Ti atoms, we observe some changes in the nature of the chemical bonding in the PZT, e.g. increasing the Zr impurity concentration enhances of the covalent nature in the chemical bonding of these materials.

REFERENCES

1. J. F. Scott and C. A. Paz de Araujo, "Ferroelectric memories," *Science* **246**, pp. 1400-1405, 1989.
2. G. H. Haertling, "Ferroelectric thin films for electronic applications," *J. Vac. Sci. Technol. A* **9**, pp. 414-420, 1991.
3. C. H. Ahn, R. H. Hammond, T. H. Geballe, M. R. Beasley, J.-M. Triscone, M. Decroux, O. Fischer, L. Antognazza, and K. Char, "Ferroelectric field effect in ultrathin SrRuO₃ films," *Appl. Phys. Lett.* **70**, pp. 206-208, 1997.
4. R. E. Cohen and H. Krakauer, "Lattice dynamics and origin of ferroelectricity in BaTiO₃: linearized-augmented-plane-wave total-energy calculations," *Phys. Rev. B* **42**, pp. 6416-6423, 1990.
5. K. M. Rabe and U. V. Waghmare, "Ferroelectric phase transitions from first principles," *J. Phys. Chem. Solids* **57**, pp. 1397-1403, 1996.
6. A. Garcia and D. Vanderbilt, "First-principles study of stability and vibrational properties of tetragonal PbTiO₃," *Phys. Rev. B* **54**, pp. 3817-3824, 1996.
7. R. E. Cohen, "Origin of ferroelectricity in perovskite oxides," *Nature* **358**, pp. 136-138, 1992.
8. K. Miura and M. Tanaka, "Electronic structures of PbTiO₃: covalent interaction between Ti and O ions," *Japan J. Appl. Phys.* **37**, pp. 6451-6459, 1998.
9. T. Tybell, C. H. Ahn, and J.-M. Triscone, "Control and imaging of ferroelectric domains over large areas with nanometer resolution in atomically smooth epitaxial Pb(Zr_{0.2}Ti_{0.8})O₃ thin films," *Appl. Phys. Lett.* **72**, pp. 1454-1456, 1998.
10. R. Guo, I. E. Cross, S.-E. Park, B. Noheda, D. E. Cox, and G. Shirane, "Origin of the high piezoelectric response in PbZr_{1-x}Ti_xO₃," *Phys. Rev. Lett.* **84**, pp. 5423-5426, 2000.
11. Y. Watanabe, "Electrical transport through Pb(Zr,Ti)O₃ p-n and p-p heterostructures modulated by bound charges at a ferroelectric surface: ferroelectric p-n diode," *Phys. Rev. B* **59**, pp. 11257-11266, 1999.
12. B. Noheda, J. A. Gonzalo, I. E. Cross, R. Guo, S.-E. Park, D. E. Cox, and G. Shirane, "Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: the structure of PbZr_{0.52}Ti_{0.48}O₃," *Phys. Rev. B* **61**, pp. 8687-8695, 2000.
13. A. Stashans, C. Zambrano, A. Sánchez, and L. M. Prócel, "Structural properties of PbTiO₃ and PbZr_xTi_{1-x}O₃: a quantum chemical study," *Int. J. Quant. Chem.* **87**, pp. 145-151, 2002.
14. A. L. Shluger and E. V. Stefanovich, "Models of the self-trapped exciton and nearest-neighbor defect pair in SiO₂," *Phys. Rev. B* **42**, pp. 9664-9673, 1990.
15. L. Kantorovich and A. Livshits, "A novel approach for constructing symmetry-adapted basis sets for quantum-chemical calculations," *Phys. Status Solidi (b)* **174**, pp. 79-90, 1992.
16. R. A. Evarestov and V. A. Lovchikov, "Large unit cell calculations of solids in the CNDO approximation," *Phys. Status Solidi (b)* **97**, pp. 743-751, 1979.
17. R. A. Evarestov, *Quantum-Chemical Methods of Solid State Theory*, Leningrad State University Press, Leningrad, 1982.
18. A. Stashans and M. Kitamura, "A study of a hydrogen doped semiconductors using the INDO method," *Solid State Commun.* **99**, pp. 583-588, 1996.
19. S. Lunell, A. Stashans, L. Ojamäe, H. Lindström, and A. Hagfeldt, "Li and Na diffusion in TiO₂ from quantum chemical theory versus electrochemical experiment," *J. Am. Chem. Soc.* **119**, pp. 7374-7380, 1997.
20. P. Persson, A. Stashans, R. Bergström, and S. Lunell, "Periodic INDO calculations of organic adsorbates on a TiO₂ surface," *Int. J. Quant. Chem.* **70**, pp. 1055-1066, 1998.
21. A. Stashans, S. Lunell, R. Bergström, A. Hagfeldt, and S.-E. Lindquist, "Theoretical study of lithium intercalation in rutile and anatase," *Phys. Rev. B* **53**, pp. 159-170, 1996.
22. A. Stashans and M. Kitamura, "Hydrogens in semiconductors," *J. Phys. Chem. Solids* **58**, pp. 777-787, 1997.
23. A. Stashans, S. Lunell, and R. W. Grimes, "Theoretical study of perfect and defective TiO₂ crystals," *J. Phys. Chem. Solids* **57**, pp. 1293-1301, 1996.
24. A. Fahmi, C. Minot, B. Silvi, and M. Causà, "Theoretical analysis of the structures of titanium dioxide crystals," *Phys. Rev. B* **47**, p. 11717-11724, 1993.
25. A. Stashans, E. Kotomin, and J.-L. Calais, "Calculation of the ground and excited states of F-type centers in corundum crystals," *Phys. Rev. B* **49**, pp. 14854-14858, 1994.
26. L. Kantorovich, A. Stashans, E. Kotomin, and P. W. M. Jacobs, "Quantum chemical simulations of hole self-trapping in semi-ionic crystals," *Int. J. Quant. Chem.* **52**, pp. 1177-1198, 1994.
27. E. A. Kotomin, A. Stashans, and P. W. M. Jacobs, "Modelling of point defects in α -Al₂O₃," *Rad. Eff. Def. Solids* **134**, pp. 87-90, 1995.
28. A. Stashans and S. Lunell, "Semiempirical calculations of WO₃ and M_xWO₃ crystals (M= H, Li, Na) ," *Int. J. Quant. Chem.* **63**, pp. 729-735, 1997.

29. R. I. Eglitis, M. M. Kuklja, E. A. Kotomin, A. Stashans, and A. I. Popov, "Semi-empirical simulations of the electronic centres in MgO crystal," *Comput. Mater. Sci.* **5**, pp. 298-306, 1996.
30. L. Patthey, H. Rensmo, P. Persson, K. Westermarck, L. Vayssieres, A. Stashans, Å. Petersson, P. A. Brühwiler, H. Siegbahn, S. Lunell, and N. Mårtensson, "Adsorption of bi-isonicotinic acid on rutile TiO₂ (110)," *J. Chem. Phys.* **110**, pp. 5913-5918, 1999.
31. R. I. Eglitis, A. V. Postnikov, and G. Borstel, "Semi-empirical Hartree-Fock calculations for KNbO₃," *Phys. Rev. B* **54**, pp. 2421-2427, 1996.
32. E. A. Kotomin, R. I. Eglitis, A. V. Postnikov, G. Borstel, and N. E. Christensen, "First-principles and semi-empirical calculations for bound-hole polarons in KNbO₃," *Phys. Rev. B* **60**, pp. 1-5, 1999.
33. R. I. Eglitis, E. A. Kotomin, and G. Borstel, "Quantum chemical modelling of perovskite solid solutions," *J. Phys.: Condens. Matter* **12**, pp. L431-L434, 2000.
34. A. Stashans and H. Pinto, "Hole polarons in pure BaTiO₃ studied by computer modeling," *Int. J. Quant. Chem.* **79**, pp. 358-366, 2000.
35. H. Pinto and A. Stashans, "Quantum-chemical simulation of Al- and Sc-bound hole polarons in BaTiO₃ crystal," *Comput. Mater. Sci.* **17**, pp. 73-80, 2000.
36. H. Pinto, A. Stashans, and P. Sánchez, *Defects and Surface-Induced Effects in Advanced Perovskites*, NATO Science Series, High Technology, Vol. 77, p. 67, Kluwer Academic Publishers, Dordrecht, 2000.
37. E. Patiño and A. Stashans, "Structural and electronic effects in BaTiO₃ due to the Nb doping," *Ferroelectrics* **256**, pp. 189-200, 2001.
38. A. Stashans and P. Sánchez, "A theoretical study of La-doping in strontium titanate," *Mater. Lett.* **44**, pp. 153-157, 2000.
39. A. Stashans, "Quantum-chemical studies of free and potassium-bound hole polarons in SrTiO₃ cubic lattice," *Mater. Chem. Phys.* **68**, pp. 124-131, 2001.
40. A. Stashans, F. Erazo, J. Ortiz, and P. Valverde, "Oxygen-vacancy defects on the SrTiO₃ (001) surface: a quantum-chemical study," *Phil. Mag. B* **81**, pp. 1977-1988, 2001.
41. P. Sánchez and A. Stashans, "Computational study of structural and electronic properties of superconducting La-doped SrTiO₃," *Phil. Mag. B* **81**, pp. 1963-1976, 2001.
42. A. Stashans and S. Serrano, "A quantum-chemical study of polar SrTiO₃ (110) surface and oxygen-vacancy defects therein," *Surf. Sci.* **497**, pp. 285-293, 2002.
43. F. Erazo and A. Stashans, "Quantum-chemical studies of Nb-doped CaTiO₃ crystal," *Phil. Mag. B* **80**, pp. 1499-1506, 2000.
44. F. Erazo and A. Stashans, "Structural and electronic properties of La-doped CaTiO₃ crystal," *Int. J. Quant. Chem.* **87**, pp. 225-231, 2002.

Correspondence: Email: alfredox@hotmail.com; Fax: +593-2-2401583