


# ANALYSIS OF THE STRUCTURAL PROPERTIES IN ERBIUM DOPED BARIUM TITANATE BY MOLECULAR DYNAMICS SIMULATIONS

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## ● Resumen

La simulación atómica ha sido empleada para estudiar mecanismos de incorporación del Erblio en la estructura cristalina del titanato de bario. Los resultados estáticos y dinámicos de las simulaciones predicen la existencia de un nuevo mecanismo de incorporación; el cual sugiere la existencia de este mecanismo mixto de auto-compensación de cargas, como una fuente adicional de vacancias de oxígeno en la estructura cristalina, y otro posible origen de la anomalía dieléctrica presente en este material.

Palabras clave: titanato de bario, microestructura, mecanismo de Incorporación.

## ● Abstract

Atomic simulation has been used to study mechanisms of incorporation of the Erbium in the crystalline structure of Barium Titanate. The static and dynamic aftermath of simulations predict the existence of a new mechanism of incorporation; which suggests the existence of this mixed mechanism of car compensation of loads, like an additional source of vacancies of oxygen in the crystalline structure, and another possible origin of dielectric anomaly present in this material.

Keywords: barium titanate, microstructure, incorporation mechanism.

## ● Introduction

Barium Titanate (BT) is one of the most widely used ceramic materials in the electronic industry. Er<sup>3+</sup>-doped Barium Titanate has received attention for its IR-to-visible frequency conversion and potential application in luminescent devices /1, 2/. BT has a perovskite structure made upon a framework of corner linked TiO<sub>2</sub> octahedral with centrally occupied Ba<sup>2+</sup> ions. The intrinsic facility to host ions of different sizes is of fundamental importance in tailoring its ultimate properties. The influence of the dopant ion depends on the substitution site (Ba<sup>2+</sup> or Ti<sup>4+</sup>) as well as on the defect(s) required for charge compensation in the lattice.

The ionic radius of the dopant ion is essential in determining the substitution site /3, 4/. Large ions,

such as La<sup>3+</sup> and Nd<sup>3+</sup>, give exclusive substitution at the Ba<sup>2+</sup> site (1.35 Å), as their size is far too large respect to the Ti<sup>4+</sup> sites (0.68 Å) and would cause the perovskite structure to become unstable /5, 6/. Ions with intermediate size such as Y<sup>3+</sup> and Er<sup>3+</sup> can substitute on both crystallographic cation sites.

Atomistic simulations have shown the predominant mechanism corresponding to cations with intermediate ionic radius size, such as Er<sup>3+</sup>, is the self-compensation mechanism /7/.

Lewis and Catlow /8/ used lattice statics methods to study the defect chemistry of doped and undoped barium titanate for multiple dopant types. Many properties were satisfactorily reproduced including the lattice (cohesive) energy, elastic constant, optical and static dielectric constants and the formation and

migration energies of the lattice defects /8-10/. A similar study was later performed by Buscaglia *et al.* /7/. In this work were considered four incorporation mechanisms and the most experimentally commonly reported dopants were featured. For larger

La<sup>3+</sup> and Pr<sup>3+</sup>) they reported Ba<sup>2+</sup> site substitution with electron compensation, for intermediate sized cations (e.g. Gd<sup>3+</sup>, Tb<sup>3+</sup> and Er<sup>3+</sup>) the self-compensation reaction occurs predominantly. Also they were found that the Ti<sup>4+</sup> vacancy compensation scheme (donor case) to be energetically unfavorable for all the cations studied. Unexpectedly, they found the binding energies of these generally highly charged defects to have small negative or even positive values. However the incorporation mechanism of Er<sup>3+</sup>-doping, in the BT lattice structure, at 1 mole %, is not yet clear.

The aim of this work is to study a possible incorporation mechanism for 1% mol Er<sup>3+</sup>-doped Barium Titanate, using lattice static and dynamic techniques.

### ● Simulation procedure

The incorporation mechanism of the impurity in BT lattice is an important factor that determines the nature of atomic interactions, diffusion and conduction behavior in this material.

Oxygen vacancies ( $V_{O}^{\bullet\bullet}$ ) in perovskite structures in general are the only point defect with significant mobility. Experimental evidence of measurements of electric conductivity for the doped and pure BT showed that the formation of hole-electron defects type, as a charge compensation mechanism, is subversive in comparison to oxygen vacancies /11, 12/.

One of the characteristics more common in BT modified with Er<sup>3+</sup> is the presence of the diffuse dielectric anomaly above the Curie temperature 700-1000K, where the material undergoes in paraelectric phase /13, 14/. The fundamental origin of this anomaly is the presence of certain amount of oxygen vacancies in the material.

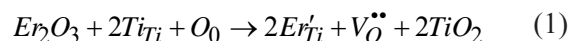
Buscaglia *et al.* /15/ were reported the evolution of the microstructure, unit cell parameters and room-

temperature resistivity of BT ceramics doped with Er<sup>3+</sup> as a function of dopant concentration, and the Ba/Ti molar ratio. They proposed a compensation mechanism when the Ba/Ti > 1 at 2 mol % Er<sup>3+</sup> doped to adapt the excess negative and positive charges.

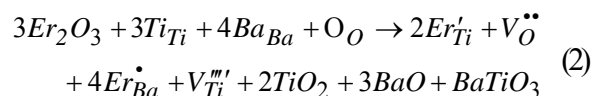
In this work only two incorporation mechanisms were considered: the acceptor mechanism and our new mechanism labeled the mixed self-compensation mechanism (or simply mixed), where the Er<sup>3+</sup> is placed into Ba sites, compensating the excess positive charge with titanium vacancies ( $V_{Ti}^{\prime\prime\prime}$ ) and also as an acceptor with oxygen vacancies.

This scheme is a potential source of oxygen vacancies that is not present in previous self-compensation mechanisms.

For Er<sup>3+</sup>-dopant incorporation, charge compensation can occur either by anion vacancies (acceptor) according to reaction equations:



Consequently one oxygen vacancy is created when two Er<sup>3+</sup> ions substitute at two Ti<sup>4+</sup> sites. For the mixed case the reaction-equation is:



Also one oxygen vacancy is created when two Er<sup>3+</sup> ions substitute at two Ti<sup>4+</sup> sites and one titanium vacancy is created after four Er<sup>3+</sup> ions substitute at two Ba<sup>2+</sup> sites. The simulated cell for the acceptor case consists of 198 Ti<sup>4+</sup>, 200 Ba<sup>2+</sup>, 2 Er<sup>3+</sup>, 599 O<sup>2-</sup> (one  $V_{O}^{\bullet\bullet}$ ), and for the mixed 597 Ti<sup>4+</sup> (one  $V_{Ti}^{\prime\prime\prime}$ ), 596 Ba<sup>2+</sup>, 6 Er<sup>3+</sup> (four in the Ba<sup>2+</sup> site and two in the Ti<sup>4+</sup> site), 1799 O<sup>2-</sup> (one  $V_{O}^{\bullet\bullet}$ ).

Interatomic potentials have long been used with considerable success to describe ionic materials and perovskite ferroelectrics /7, 8, 10, 17-19/. One of the most types of potential used to define short-range interactions for ionic materials is the Buckingham potential, which takes the form:

$$V_{ij}(r_{ij}) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (3)$$

where  $A_{ij}$ ,  $\rho_{ij}$ , and  $C_{ij}$  are potential parameters for a pair of ions  $i$  and  $j$ , and  $r_{ij}$  is the distance between

them. The exponential term of the short-ranged Buckingham potential takes account of Pauli repulsion, whereas the  $r^{-6}$  term takes account of the attractive dispersion or Van Der Waals interaction. The potential parameter derived by Buscaglia *et al.* [7] were used to modeling all pair interaction. All calculations were performed in GULP3.4 code [20].

### ● Results and discussions

The minimum lattice energy procedure was used to calculate the most accurate system according to the lattice properties. In order to examine the effect of concentration of point defects in the material, is necessary to find out the configuration of minimal energy regarding the atomic coordinates under constant external pressure equal to 0 GPa. For this method it is possible to know the lattice (cohesive)

energy and other structural properties for each simulation box constructed from the equations (1) and (2), respectively. Cohesive energy and the lattice parameters of both resulting solids were calculated to ensure that the mixed mechanism can be (or not) replicate the solid structure of BT.

Figure 1 shows the lattice energy and their respectively cell parameters from each incorporation mechanism. The mixed case is the best closed respect to the lattice energy value for the perfect BT (-148,02 eV). When the energy difference between two incorporations mechanism is small, such as happened in this case, them is possibly that one of both can be occur with the same occurrence probability. But while more negative is the cohesive energy them the solid structure is more stable, so the mixed is a structure more stable than acceptor.

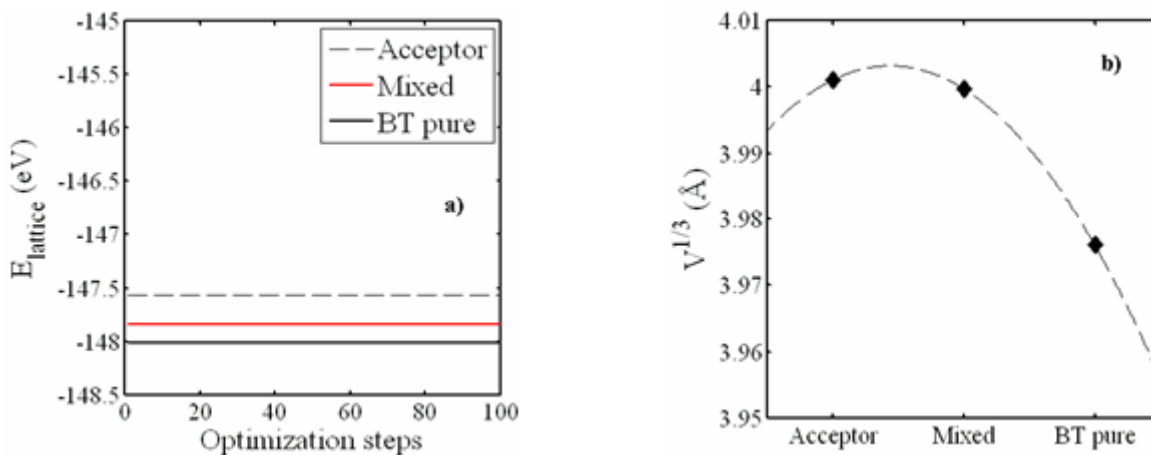


Fig. 1 Cohesive energy a) and unit cell parameter b) for simulation box of the acceptor and mixed Er<sup>3+</sup>-incorporation mechanisms, respectively.

The mixed case is more stable than acceptor incorporation mechanism.

The cohesive energy of both systems is higher respect to the BT pure, indicating a structural expansion respect to the undoped BT as shown in the Figure 1 b) and Table 1.

TABLE 1. STRUCTURAL PROPERTIES OF 1% ER-DOPED BT OBTAINED BY THE ENERGY MINIMIZATION CRITERION

1% Er-BT	$E_L$ (eV)	$V^{1/3}$ (nm)	Ref. 11
Acceptor	-146,56	0,400 1	0,400 05 - 0,400 20
Mixed	-147,84	0,400 0	
Undoped BT	-148,02 <sup>8</sup>	0,396 <sup>11</sup>	

In order to clarify how the structural properties are affected by these foreign ions, including their incorporation mechanism, and the possible disorder, the radial distribution functions, recurrently used to investigate this effect [18, 19], of each simulated solid were calculated by the equation:

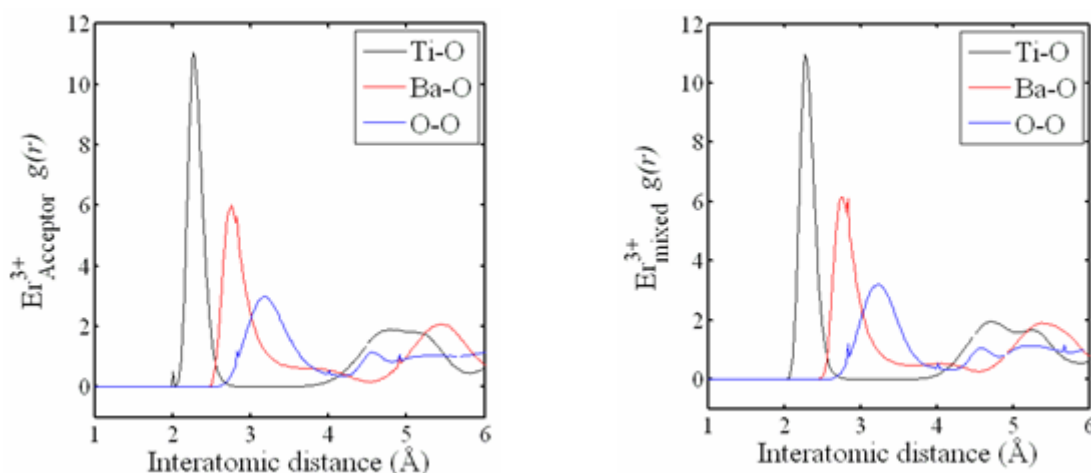
$$g_{ij}(r) = \frac{1}{4\pi r^2 dr} \frac{n_{ij}(r)}{\rho_j} \quad (4)$$

where  $n_{ij}(r)$  is the number of particles of type  $j$  located at a distance between  $r$  and  $r + dr$  from a

particle of type  $i$  and  $\rho_j$  is the number density of particles of types  $j$ .

A short dynamic simulation was performed at 300 K for the acceptor, mixed and BT perfect perovskite structure, under constant temperature-pressure ensemble with external pressure of 0 GPa. Newton's equation of motion was integrated until 1 ns with time step of 1 fs were the means square displacement for the oxygen atoms was recorded each 0,1 ps. Andersen

thermostat /21/ was applied to rescale the velocity of one oxygen ion, selected randomly, at time, with collision ratio of 1. Berendsen barostat /22/ was employed to controller the pressure with constant decay of 0.1 ps. Ewald summation method<sup>23</sup> have been used to calculate the electrostatic terms of potential using the formal charges of barium, titanium, erbium and oxygen ions of which values are +2, +4, +3 and -2, respectively, short-range potential cut-off is set to 0,12 nm.



**Fig.2 Radial function distribution,  $g_{ij}(r)$ , of acceptor (up) and mixed (down) incorporation mechanism. The results confirm the stability of the perovskite structure in both simulation boxes.**

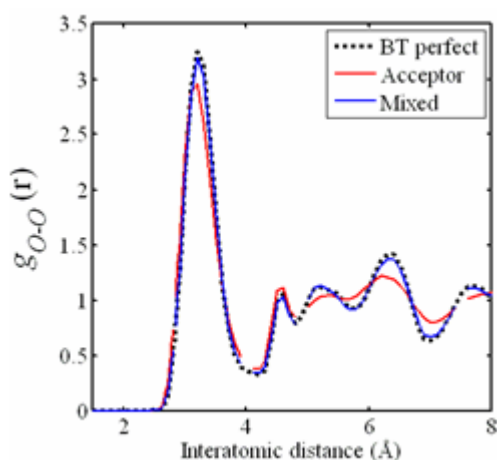
With the obtained trajectories the oxygen-oxygen radial function distribution,  $g_{ij}(r)$ , from each solid are shown in the Figure 3. We were checked that the perovskite structure is maintained by each pair-ion,  $g_{ij}(r)$ , proving so that the mixed self-compensation mechanism is possible that occur as doping-process.

The disorder character of anion sublattice can be studied from the oxygen-oxygen radial distribution function,  $g_{O-O}(r)$ , taken from a room temperature for each system (according to each incorporation mechanism). They were compared with those expected from a perfect BT perovskite structure with the same lattice parameter. In the Figure 3 are shown the results. Comparing (qualitatively) the position of the first pick (or first coordination sphere) of each  $g_{O-O}(r)$ , and the dispersion observed after the 4 Å, the mixed mechanism, induces less structural disorder in comparison with the acceptor case. The height of the first pick from the acceptor is smaller than the corresponding to the perfect BT and mixed

cases, and it presents higher space dispersion (respect to the inter-atomic distance). These results suggest that the mobility of the oxygen ions for the acceptor case is more substantial respect to the mixed one, consequently is required smaller activation (migration) energy to move the mobile anion-species in the structure. This result confirms that the oxygen-vacancies generated by the mixed mechanism can be alternative source of the dielectric anomaly of 1 % Er-BaTiO<sub>3</sub> up to ~120 °C.

In resume, the acceptor incorporation mechanism can creates weaker Er-O interactions compared to the Ti-O. The binding energy of defect pairs ( $2Er_{Ti}^{\prime}, V_{O}^{\bullet\bullet}$ ) results in the failure of Er-O interaction rather than a Ti-O interaction which is inferior in energy. Other authors have reported the binding energy becomes more negative with increasing ionic radii of the RE dopant as consequence of the size difference between the RE ion and the Ti<sup>4+</sup> ion /7, 10/. Its produces a strong interaction between

oxygen vacancies and the  $\text{Er}^{3+}$  sites due to the close binding arrangement formed by the  $\text{TiO}_2$  octahedral, and the volume of this octahedral is affected. The mixed self-compensation mechanism consists of a multiple-complex defects, constituted by  $(4\text{Er}_{\text{Ba}}^{\bullet}, 2\text{Er}_{\text{Ti}}^{\bullet})^{\bullet\bullet}$ ,  $(V_{\text{Ti}}^{\bullet\bullet}, V_{\text{O}}^{\bullet\bullet})$  in general for this mechanism can be some types of alternatives formation of pair defects. The interactions between these defects will be strong, because the addition of possible binding energies from other mechanisms that generates a hard electrostatic interaction between them.



**Fig. 3** Radial function distribution of  $\text{O}^{2-}\text{-O}^{2-}$  pair of each system obtained by acceptor and mixed incorporation mechanism compared with BT perfect. The acceptor behavior creates more anionic disorder in the lattice structure.



## Conclusions

*Atomistic simulations have been used to study the lattice properties of 1% mol of  $\text{Er}^{3+}$ -doped barium titanate. The cohesive energy calculations of the various incorporation mechanisms of  $\text{Er}^{3+}$  onto BT structure shows that mixed mechanism is the predominant mechanism.*

*The radial function distribution analysis corroborates the fact of the structural properties are correctly reproduced by the mixed self-compensation mechanism than acceptor case. It has been shown that the mixed self-compensation mechanism is definitely a possible incorporation mechanism for this rare-earth ion.*

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## Bibliography

- PATRA A., Friend; C. S. R. KAPOOR, P. N PRASAD. "Fluorescence up Conversion Properties of  $\text{Er}^{3+}$  Doped  $\text{TiO}_2$  and  $\text{BaTiO}_3$  Nanocrystales". *J. Chem. Mater.* 2003, 15, 3650-3655.
- KUO, S. Y.; C. S. CHEN; T. Y. TSENG; S. C. CHANG; W. F. HSIEH. "Dependence of Luminescence Efficiency on Dopant Concentration and Sintering Temperature in the Erbium Doped  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  thin Films". *J. Appl. Phys.* 2002, 92, 1868-1872.
- XUE, L.A.; Y. CHEN; R. BROOK. "The Influence of Ionic-Radii on the Incorporation of Trivalent Dopants into  $\text{BaTiO}_3$ ". *J. Mater. Sci. Eng.* B1. 1988, 193-201.
- BUSCAGLIA, M. T.; V. BUSCAGLIA; M. VIVIANI; P. NANNI; M. HANUSKOVA. "Influence of Foreign Ions on the Crystal Structure of  $\text{BaTiO}_3$ ". *J. Eur. Ceram. Soc.* 2000, 20, 1997-2007.
- ROTH, R. S. "Classification of Perovskite and other  $\text{ABO}_3$ -Type Compounds". *J. Res. Natl. Bur. St.* 1957, 58, 75-88.
- SHANNON, R. D. "Synthesis of Some New Perovskites Containing indium and thallium". *Inorg. Chem.* 1967, 6, 1474-1478.
- BUSCAGLIA, M. T.; V. BUSCAGLIA; M. VIVIANI; P. NANNI. "Atomistic Simulation of. Doped Incorporation in Barium Titanate". *J. Am. Ceram. Soc.* 2001, 84, 376-384.
- LEWIS, G. V.; R. A. Catlow C. "Defect Studies of Doped and Undoped Barium Titanate Using Computer Simulation Techniques". *J. Phys. Chem. Solids.* 1986, 4, 89-97.
- DONNERBERG, H. J.; S. M. TOMLINSON; R. A. CATLOW C. "Defects  $\text{LiNbO}_3$  Computer Simulation". *J. Phys. Chem. Solids.* 1991, 52, 201-210.
- FREEMAN, C. L. *et al.* "A New Potential Model for Barium Titanate and its Implications for Rare-Earth Doping". *J. Mater. Chem.* 2011, 21, 4861-4868.
- PISKUNOV, S.; E. HEIFETS; R. I. EGLITIS; G. BORSTEL. "Bulk Properties and Electronic Structure of  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$  Perovskites: an *ab initio* HF/DFT Study". *Computational Materials Science.* 2004, 29, 165-178.
- CHAN, N. H.; R. S. SHARMA; D. M. SMYTH. "Non-Stoichiometry in undoped  $\text{BaTiO}_3$ ". *J. Am. Ceram. Soc.* 1981, 64, 556-562.
- \_\_\_\_\_. "Non-Stoichiometry in Acceptor Doped  $\text{BaTiO}_3$ ". *J. Am. Ceram. Soc.* 1982, 65, 167-170.



14. KANG, B. S.; S. K. CHOI. "Diffuse Dielectric Anomaly of BaTiO<sub>3</sub> in the Temperature Range of 400–700°C". *Solid State Commun.* 2002, 121, 441-446.
15. LEYET, Y.; F. GUERRERO; J. PÉREZ. "Relaxation Dynamics of the Conductive Processes in BaTiO<sub>3</sub> Ceramics at High Temperature". *J. Mater. Sci. Eng. B.* 2010, 171, 127-132.
16. BUSCAGLIA, M. T.; M. VIVIANI; V. BUSCAGLIA; C. BOTTINO; P. NANNI. "Incorporation Mechanism of Er<sup>3+</sup> onto BaTiO<sub>3</sub>". *J. Am. Ceram. Soc.* 2002, 85, 1569-1575.
17. DEVANTHAN, R.; W. J. WEBER; S. C. SINGHAL; J. D. GALE "Computer simulation of Defects and Oxygen Transport in Yttria-Stabilized Zirconia". *Solid State Ionics.* 2006, 177, 1251-1258.
18. LAU, K. Ch.; B. I. Dunlap. "Molecular Dynamics Simulation Of yttria-Stabilized zirconia (YSZ) Crystalline and Amorphous Solids". *J. Phys.: Condens. Matter.* 2011, 23, 035401-035417.
19. DAVIS, S.; B. A. BELONOSHKO; A. ROSENGREN; A. C. VAN DUIN; B. Johansson. "Molecular Dynamics Simulation of Zirconia Melting". *Cent. Eur. J. Phys.* 2010, 8(5), 789-797.
20. GALE, J.; A. ROHL. "The General Utility Lattice Program (GULP)". *Molecular Simulation.* 2003, 29, 291-341.
21. ANDERSEN, H. C. "Rattle: A «Velocity» Version of the Shake Algorithm for Molecular Dynamics Calculations". *J. Comput. Phys.* 1983, 52, 24-34.
22. BERENDSEN H., J. C.; J. P. POSTMA; W. F. VAN GUNSTEREN; A. DINOLA; J. R. HAAK. "Molecular Dynamics with Coupling to an External bath". *J. Chem. Phys.*, 1984, 81, 3684-3690.
23. EWALD, P. P. *Ann. Phys.* 1921, 64, 253.