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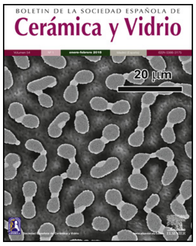

Comparative study of the phase stability in $SrTaO_2N$

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ABSTRACT

Recently, ferroelectric behavior was observed in compressed $SrTaO_2N$ thin films epitaxially grown on $SrTiO_3$ substrates. Piezoresponse force microscopy measurements revealed small domains (10^1–10^2 nm) that exhibited classical ferroelectricity, a behavior not previously observed in perovskite oxynitrides. The surrounding matrix region exhibited relaxor ferroelectric-like behavior. Bulk $SrTaO_2N$ samples do not show ferroelectricity, thus suggesting that the origin of it may be related with the strain induced by the substrate. *Ab-initio* calculations reported that the small domains and the surrounding matrix had trans-type and a cis-type anion arrangements, respectively, but do not describe the experimentally observed equilibrium phase, nor the strain dependent polarization. In this work, we present high accurate all-electron first-principles calculations on the different possible local structures that can explain the ferroelectric-like properties of the strained material. The determined local structure and oxygen/nitrogen ordering has been related with polarization and epitaxial strain. The potential energies and polarization as functions of the in-plane lattice constant are reported.

Estudio comparativo de la estabilidad de fases en $SrTaO_2N$

Palabras clave:
Ferroelectricidad
Dieléctricos
Ab-initio

RESUMEN

Recientemente, se observó comportamiento ferroeléctrico en películas delgadas de $SrTaO_2N$ crecidas epitaxialmente sobre sustratos de $SrTiO_3$. En mediciones de microscopía de fuerza piezoeléctrica se observaron pequeños dominios (10^1-10^2 nm) que exhibieron ferroelectricidad clásica. Este comportamiento no fue observado previamente en oxinitruros de perovskita. La región de la matriz circundante a estos dominios presentaron un comportamiento del tipo relaxor. En muestras macroscópicas de $SrTaO_2N$ no fue encontrada ferroelectricidad, lo que sugiere que el origen de la misma puede estar relacionado con el esfuerzo de corte inducido por el sustrato. Cálculos *ab-initio* realizados previamente parecen

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concluir que los pequeños dominios ferroeléctricos y la matriz circundante tienen disposiciones de aniones del tipo trans y cis, respectivamente, pero en ellos no se predice la fase de equilibrio observada experimentalmente, ni la polarización neta resultante en la estructura ferroeléctrica dependiente del esfuerzo de corte. En este trabajo presentamos cálculos de primeros principios de alta precisión realizados sobre las diferentes estructuras locales posibles que pueden explicar las propiedades ferroeléctricas del material bajo esfuerzo. La estructura local determinada y el ordenamiento de oxígeno/nitrógeno se han relacionado con la polarización y la deformación epitaxial. Como producto de ello se calcularon las energías potenciales y la polarización neta como funciones de la constante de la red paralela al plano de la interfase.

Introduction

In the last years AB(O,N)$_3$ oxynitrides have attracted much attention because of their novel electronic functionalities, such as high dielectric constant [1], visible light absorption [2], photocatalytic activity [3] and colossal magneto-resistance [4]. The oxynitrides are formed by the partial substitution of oxygen by nitrogen atoms into the anionic network of the ABO$_3$ perovskite-type compounds (e.g. A = Ca, Sr, Ba or lanthanide, B = Ti, Ta or Nb). The increase of negative charges are compensated with simultaneous cationic substitutions [5–8]. The replacement of some O atoms by N ones may change the color of the initially white powders, so, these compounds have potential application as safe colored pigment material to replace currently used contaminant heavy metals (Cr, Cd, Pb, etc.) containing pigments [9]. The optical properties have been extensively studied. However, the changes in bonding type and local structure that accompany the introduction of N ions may also give rise to interesting dielectric properties. The aliovalent substitution provides a mechanism for enhance the dielectric polarizability through the substitution of more polarizable ions into the lattice [10]. Furthermore, the reduced electronegativity of the N ion respect to the O one, would rise up the covalence character of the cation–anion bonds [1]. The increased covalency of the bonding can in turn increase the likelihood of cation displacements through a second-order Jahn–Teller distortion of the d^0 cation [11]. It is well known that such displacements are the origin of ferroelectricity. On the other hand, the mixed occupancy of the anion site in oxynitrides, AB(O$_{1-x}$N$_x$)$_3$, provides a condition similar to that found in relaxors, as the polarizing octahedral cations will experience random chemical environments in the absence of complete O/N ordering. It is therefore, an interesting issue to examine whether the perovskite oxynitrides possess intrinsically high κ and relaxor-like properties.

The electronic structure of perovskite oxynitrides may be influenced by the geometrical configuration of the O and N atoms around their metal cations. For the case of ABO$_2$N oxynitride, in which each B cation is surrounded by four O and two N ions thus forming a BO$_4$N$_2$ octahedron, there are two possible anion configurations: the two N ions can occupy either (i) adjacent (cis-type) or (ii) opposite (trans-type) sites. Researchers have argued that the dielectric properties of ABO$_2$N are related to anion arrangement. Page et al. [12] suggested that ferroelectricity in trans-type anion-ordered ATaO$_2$N (A = Sr, Ba) phases may be caused by the off-center displacement of Ta ions. They have used different nitrogen arrangements and space groups in order to investigate the stability of oxynitride phases based on theoretical approach. The stability energy for the trans-type phases was higher than the determined for cis-type phases. In fact, the bulk SrTaO$_2$N specimens have been confirmed to exhibit cis-type configurations with I4mcm space group [13,14]. Recently, different ferroelectric and relaxor regions were detected in thin films samples of SrTaO$_2$N epitaxially grown on a SrTiO$_3$ substrate [15,16]. The lattice mismatch between the oxynitride and the substrate is responsible of the strain parallel to the interface thus reducing the in-plane lattice constant when it is grown as thin film, favoring the stabilization of a trans-type polar P4mm ferroelectric structure [12,15].

Computational quantum-mechanical simulations have proven to be a suitable tool for understanding the microscopic processes that are responsible of the physical properties of materials. Beyond the simplicity of the models, in comparison to the complexity of real materials especially in disordered and ceramic materials, they can lead to a good description of individual processes involved. Although some previous studies on the phase stability in bulk SrTaO$_2$N have been published [12,15,17], there are still open questions regarding the calculated phase diagrams. In the work of Page et al. and Oka et al., the experimentally stable I4mcm phase appear third in order of stability taking into account the total energy at zero pressure. The phase diagram shows that the non polar I4mcm structure and the trans-polar P4mm are very close in energy. This small difference may require the use of high precision methods to resolve between.

It is well known that within the pseudopotential methods for the calculations of the electron density, the selection of the function to represent the potential of the valence electrons may play a crucial role. This problem is not present in all-electron methods. In this work, the phase stability diagram at zero pressure is discussed considering different approaches to the Density Functional Theory (DFT) [18] by means of high precision all-electrons, and also pseudopotential methods in order to compare results and interpret the phase stability diagram. Furthermore, the ferroelectric distortion in the P4mm phase was analyzed in order to study the resulting net dipole moment as a function of the in-plane lattice parameter. The paper is organized as follows: in the second section, the computational methods are described. In the third section, the

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