Computational Materials Science 103 (2015) 224–230

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Dopants and dopant–vacancy complexes in tetragonal lead titanate: A systematic first principles study

Paul Erhart [a], Karsten Albe [b]

[a] Department of Applied Physics, Chalmers University of Technology, S-412 67 Gothenburg, Sweden
[b] Institute of Materials Science, Fachbereich 11, TU Darmstadt, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany

ARTICLE INFO

Article history:
Received 13 September 2014
Received in revised form 13 February 2015
Accepted 17 February 2015
Available online 4 March 2015

Keywords:
Degradation
Electrical and mechanical loading
Defects
Doping
PZT

ABSTRACT

A systematic investigation of dopants in tetragonal lead titanate is presented by screening elements from the third period including K, Ca and all 3*d* transition metals. Formation energies and equilibrium transition states are determined by means of density functional theory calculations for both cation sites in the perovskite lattice, which allows us to discriminate between donor and acceptor type behavior. The stability of defect dipoles is determined by calculating the binding energy of transition metal-vacancy complexes. The results reveal that the tendency to substitute the Pb-site rather than the Ti-site monotonically increases going from Ti to Zn. The transition from Ti to Pb substitution depends both on the chemical equilibrium conditions and the position of the Fermi energy. This is most evident for Sc and Zn dopants that in principle can occupy both Pb- and Ti-sites depending on preparation conditions. Except for V all acceptor dopants form defect complexes with oxygen vacancies and thus can form defect dipoles causing hardening as well as aging effects. Defect dipoles involving Pb substitution and oxygen vacancies are found to be unfavorable for all dopants considered here.

1. Introduction

Ferroelectric materials exhibit a spontaneous electric polarization, whose direction can be switched by an applied electric field. Upon cooling from the sintering temperature ferroelectric ceramics undergo a phase transition from a paraelectric to a ferroelectric state, leading to the formation of domains. These domains can be reoriented by poling and result in a remanent polarization as well as dimensional changes of the ceramic [1]. Ferroelectric materials are used in transducers, filters, sensors, ultrasonic motors or actuators [2–6], but also in microelectronic devices like non-volatile ferroelectric memory components [7,8].

From a commercial point of view, the most important ferroelectric material is lead zirconate titanate (PZT), which is a solid solution of ferroelectric lead titanate and anti-ferroelectric lead zirconate. PZT exhibits a strong piezoelectric response for compositions around the morphotropic phase boundary because of the diverging piezoelectric coefficients [1]. Technically used PZT solid solutions are always doped. Dopant type and concentration determine the piezoelectric properties and influence aging as well as fatigue [9,10]. They also affect the position of the morphotropic phase boundary and the Curie temperature [11]. In acceptor doped materials Pb or Ti/Zr ions are substituted by ions with a lower valency. In this case, charge neutrality is typically obtained by compensating oxygen vacancies. Acceptor doped materials, which are also referred to as hard doped, are difficult to polarize, exhibit high coercive fields as well as small strains and are thus typically used in sensor applications. Donor doping is realized by the substitution on cation sites with ions of higher valency and typically is associated with the formation of lead vacancies [12]. Soft or donor doped materials can be more easily poled, exhibit higher strains and low coercive fields, whence they are typically used in actors [1]. Technical PZT compositions have typically both acceptor and donor doping to meet the requirements of a given application.

It is well established that in acceptor doped materials defect reactions between dopant and oxygen vacancies can occur. For the prototypical ferroelectric $BaTiO_3$ it was demonstrated by electron paramagnetic resonance measurements (EPR) more than three decades ago [13] that $(Mn''_{Ti} - V^{\bullet\bullet}_O)^{\times}$ associates are present in reduced crystals, having an excess orientation parallel to the spontaneous polarization [14–16]. Also in lead based perovskites defect complexes, such as $(Cu''_{Ti/Zr} - V^{\bullet\bullet}_O)^{\times}$ [17,18] and $(Fe'_{Ti/Zr} - V^{\bullet\bullet}_O)^{\bullet}$, were identified by electron spin resonance (ESR) data and electronic structure calculations [19–25]. These impurity-vacancy associates as well as di-vacancies carry a dipole moment [26]. In tetragonal $PbTiO_3$ acceptor-vacancy associates can assume two different

E-mail addresses: erhart@chalmers.se (P. Erhart), albe@mm.tu-darmstadt.de (K. Albe)

http://dx.doi.org/10.1016/j.commatsci.2015.02.029
0927-0256/

arrangements with respect to the direction of the spontaneous polarization. Oxygen vacancies in one of the four equatorial positions of the oxygen octahedra generate defect dipoles perpendicular to the spontaneous polarization, whereas $V_O^{\bullet\bullet}$ in the apical oxygen positions form defect dipoles collinear to the orientation of spontaneous polarization. Identical arrangements were also found in (La,Fe) co-doped PZT [27]. Non-switching defect dipoles impose a restoring force for reversible domain switching [28]. The presence of acceptor-vacancy defect associates is thus considered the main cause for hardening in PZT ceramics. Since their gradual re-orientation is determined by the barrier for oxygen vacancy migration, these defect complexes cannot immediately follow the polarization switching [29].

While there is no doubt about the existence of vacancy-acceptor pairs at ambient conditions, much less is known about their thermodynamic stability. Temperature dependent ESR measurements on Fe-doped $SrTiO_3$ [30] revealed that iron-vacancy associates have a binding energy of −0.22 eV and dissolve at elevated temperatures, which was also found in a recent theoretical study on doped $SrTiO_3$ [31].

For $PbTiO_3$ binding energies have been calculated for complexes of Cu''_{Ti} with oxygen vacancies for various positions (see Fig. 1) [22,29]. Vacancies in the first neighbor shell of the dopant have binding energies in excess of −0.5 eV. Thus, the dissociation reaction $(Cu''_{Ti} - V_O^{\bullet\bullet})^{\times} \rightleftharpoons Cu''_{Ti} + V_O^{\bullet\bullet}$ is fully on the left hand side at ambient conditions.

The ability to observe the presence and alignment of defect dipoles in ferroelectrics by EPR has had a pronounced impact on the understanding of doping and materials degradation over time. Many dopants are, however, no detectable in EPR measurements and a direct quantitative analysis of defect concentrations and mobilities is experimentally challenging. Thus, in the search of new or alternative dopants one has to rely on intuition and/or empirical rules. If *a priori* assumptions have been made on defect positions, oxidation states and neutrality conditions, the defect chemistry of perovskites can be discussed in the framework of the Brouwer approximation [32,33]. Similarly, the treatment of defect chemistry in complex oxides by means of atomistic models using classical interatomic potentials is possible (see e.g., Refs. [34–36]), but does not allow to describe the coupling of the defect's charge state to the Fermi energy in the respective material.

However, with the advent of accurate and efficient electronic structure methods that allow the calculation of defect formation energies of individual, differently charged defect configurations, a conceptually more fundamental approach is available for addressing the problem of defect equilibria in metal oxides (see e.g., Refs. [37–42]).

In this paper, we investigate the full series of 3*d* transition metals as dopants in $PbTiO_3$ and also consider the 4*s* elements K and Ca from the first and second group of the same period. Based on electronic structure calculations within density functional theory, we calculate formation energies of differently charged states of dopants on A and B-sites of the perovskite lattice, determine equilibrium transition levels, as well as association energies of vacancy–dopant complexes.

2. Methodology

2.1. Total energy calculations

Calculations were carried out within density functional theory as implemented in the Vienna ab initio simulation package [43–46]. The ion cores and core electrons were described using the projector augmented wave method [47,48]. For transition metals semi-core states were explicitly included. The plane-wave energy cutoff was set to 500 eV. The exchange–correlation potential was represented using the local spin density approximation (LSDA).[1] All defect calculations were carried out at constant volume using $2 \times 2 \times 3$ supercells (60 atoms in the ideal cell). Brillouin zone integrals were evaluated using a non-shifted $4 \times 4 \times 4$ Monkhorst–Pack mesh.

2.2. Defect formation energy

Defect formation energies were obtained using [49]

$$\Delta E_D = (E_D - E_H) - q(\epsilon_{\mathrm{VBM}} + \mu_e) - \sum_i \Delta n_i \mu_i, \tag{1}$$

where μ_i is the chemical potential of component *i*. Here, Δn_i denotes the difference in the number of atoms of element *i* between the cell with and without the defect, e.g., for an isolated oxygen vacancy $\Delta n_O = -1$ whereas all the other Δn_i are zero. E_D is the total energy of the supercell containing the defect and E_H is the total energy of the ideal reference cell. The defect formation enthalpy is linearly dependent on the defect charge state q and the electron chemical potential μ_e which is measured with respect to the valence band maximum ϵ_{VBM}.

At this point it is important to note that the chemical potential of each constituent species depends on the thermodynamic environment. If the metal oxide MO is in equilibrium with an oxygen vapor, the chemical potential of every constituent is varying with the oxygen partial pressure and therefore also the defect formation energy (see Fig. 2).

The range of variation of the chemical potentials is, however, restricted by the stability of the phase of interest. Therefore, one can rewrite Eq. (1) by taking into account the difference between the number of atoms of type *i* in the reference cell with respect to the defective cell Δn_i, respectively. Then the chemical potential μ_i of each constituent *i* can be rewritten as $\mu_i = \mu_i^{bulk} + \Delta\mu_i$, where μ_i^{bulk} denotes the chemical potential of the standard reference state and is equivalent to the cohesive energy per atom at $T = 0$ K.

The supercell approximation introduces systematic errors due to periodic image interactions. The formation energies presented in the following were therefore corrected for potential alignment effects (see e.g., Ref. [50]) using the approach described in Ref. [51]. Image charge interactions were accounted for using the simplified correction scheme outlined in Ref. [50], which is based on a scaled monopole–monopole correction.

The computational parameters used in this work are similar to previous studies (see e.g., Refs. [21,22,40,52]). In comparison with Refs. [22,40] the supercells employed in the present study are relatively small. It must be stressed, however, that the objective of the present work is to compare a large number of different impurities in order to reveal systematic trends. The error due to the limited size of the supercells is estimated to be on the order of 0.1–0.2 eV.

The more serious shortcoming of the present approach is the band gap underestimation, which is very well known for LSDA calculations. While in principle hybrid functionals yield band gaps in much better agreement with experiment [53,54], they are also computationally much more expensive, whence they have not been used in the present context. For consistency in the analysis of the defect formation energies, which according to Eq. (1) depend on the electron chemical potential, only the calculated band gap is used.

[1] For many materials the spin-polarized generalized gradient approximation is superior to the LSDA. In the case of ferroelectric perovskites, however, it has been repeatedly observed that the LSDA yields better agreement with experiment with respect to structural and ferroelectric properties.