Charge-Carrier Enrichment at BaZrO₃/SrTiO₃ Interfaces

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Abstract

Heterogeneous doping through nano-structuring has been demonstrated to greatly enhance the transport and mass storage properties of halides and Li-ion conductors by decoupling of charge-compensating species. In this contribution, we explore the potential of heterogeneous doping of ionically conducting oxides through first principles and thermodynamic calculations of a model system consisting of acceptor-doped SrTiO₃ and BaZrO₃. We show that the two dominating defects, $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, are thermodynamically favored in BaZrO₃ compared to SrTiO₃ by 0.64 and 0.56 eV, respectively – in turn leading to an electrostatic potential barrier as large as 0.64 V (relative to BaZrO₃) at 800 K. $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, and electron holes as such accumulate on the BaZrO₃ side of the interface, leading to a charge-depletion layer in SrTiO₃, which thus acts as a heterogeneous acceptor for BaZrO₃. These interface effects may as such be used to drastically enhance the charge-carrier concentration of weakly doped ionic systems which in turn may lead to novel nanostructured composite materials with enhanced transport properties or for instance kinetics for oxygen reduction or water splitting.

1. Introduction

Interfacial effects give rise to a variety of interesting phenomena in functional materials, such as enhanced conductivity in ionic solids,¹ ferromagnetism in nonmagnetic materials,² metallicity³ and superconductivity in electrical insulators⁴. Interface effects may become dominant when the particle size is reduced to the nano-domain, both due to decreased diffusion length and increased interface-to-bulk volume ratio. The importance of such effects can be illustrated by considering one of the simplest types of interfaces; grain boundaries, which represent a structural discontinuity where chemical properties can differ from those in bulk. In many oxygen deficient and commonly acceptor-doped oxides, grain boundary cores are positively charged due to accumulation of oxygen vacancies.⁵⁻⁸ In order to maintain electroneutrality, adjacent charge-compensating space-charge zones are formed, where the concentration of oxygen vacancies and electron holes is depleted, while that of electrons is enhanced. Consequently, the DC ionic conductivity in polycrystalline

oxides is typically orders of magnitude lower than anticipated from bulk conductivity. However, reducing the particle size to a few nm may lead to orders of magnitude increase in the total conductivity due to the grain boundary induced enhancement of the n-type conductivity, as has been observed in Gd-doped CeO₂.⁹ In a sense, the grain boundary acts as a structural *donor dopant* leading to deviations from the local electroneutrality imposed by the *homogenous acceptor dopant* (Gd'_{Ce}). In general, any aperiodicity in an otherwise periodic crystalline lattice, such as surfaces, dislocations, and domain boundaries, affects the chemistry of the lattice sites and may lead to effective doping. The same applies to interfaces between different materials, offering more flexibility in tailoring the defect structure of the interface through the physicochemical properties of the two bulk phases, leading to effectively *heterogeneously doped* nanocomposites. In such two-phase systems, heterogeneous doping may result in considerable separation of dopants and charge carriers, consequently eliminating the effect of defect association that otherwise lowers the mobility of charge carriers in *e.g.* H⁺, O²⁻ and Li⁺ conductors.¹⁰⁻¹³

Heterogeneous doping has been explored for several halide systems, typically sharing a common cation or anion, as in for instance BaF₂/CaF₂, where lattice ions segregate across the interface forming mobile interstitial defects in one phase and vacant lattice sites in the other. The extent of the doping effect is determined by the thermodynamics of heterogeneous defect reactions of common species, which in the case of BaF₂/CaF₂¹⁴⁻¹⁵ is

It is worth noting that we deliberately let the equation break the common principle of restricting defect chemistry and balancing effective charges to only one phase. Here, the shift of defect-originated charge from one side to the other is the central principle. The driving force for defect segregation is the difference in the chemical potential of charged species in the two phases, which can be divided into the standard chemical potential and an activity dependent component.

Near the interface, the defect concentration can be significant, and yield ionic conductivities orders of magnitude higher than that of the bulk phases as shown for layered structures and composites of BaF₂/CaF₂¹⁴ and AgCl/AgI¹⁶. Moreover, the availability of two phases with widely different electronic and defect structure can allow so-called *job-sharing* storage of chemical species. Such storage has been demonstrated in composites of Ru and Li₂O, where excess Li is stored separately as e⁻ in Ru and interstitial Li⁺-ions in Li₂O.¹⁷ The same composite was reported to store H₂ as e⁻ or H⁻ in Ru and H⁺ in Li₂O.¹⁸ Except for these examples, only a handful of studies exist on job-sharing storage of H-related species and the chemistry of interfaces in systems where at least one of the constituents is a proton conducting oxide. Polfus *et al.*¹⁹ considered the heterogeneous interface between BaZrO₃ and MgO, showing that v_O^{••} and OH_O[•] are depleted at the BaZrO₃ side of the interface due to accumulation of protons at the first plane in MgO. The role of segregation of v_O^{••} and OH_O[•] from the bulk-like layers of MgO to BaZrO₃ was neglected, despite of both defects exhibiting favorable bulk-to-bulk segregation thermodynamics. In nanocomposites of CsHSO₄ and TiO₂, Chan *et al.*²⁰ reported that space-charge formation due to segregation of H⁺ from the solid acid to TiO₂ promoted superionic transition in CsHSO₄ at much lower temperatures than in the pure phase. The existence of such space-charge layer was later confirmed in a density functional

theory (DFT) study by Haverkate *et al.*²¹. As in the halides, a single chemical species (here H^+) is involved in the heterogeneous defect reaction

Yang *et al.*²² and Foglietti *et al.*²³ studied the spatially resolved electrical conductivity of the interface between Y-doped $BaZrO_3$ films deposited on $NdGaO_3$, revealing significantly higher conductivities with lower activation energy near misfit dislocations than in bulk-like regions. The authors, however, ascribed this behavior to strain effects, rather than space-charge formation. It is worth to mention that, contrary to the heterointerfaces between $BaZrO_3$ and $SrTiO_3$, the pristine surfaces of these materials have been addressed by numerous computational studies.²⁴⁻²⁵

In contrast to halides, where the heterogeneous doping effect is determined (and limited) by the segregation of a single species, the complex defect structure of oxides may result in widely different defect structures at the interface depending on the dominating defect disorder of the two oxides, and their relative chemistries. To the best of our knowledge, no studies exist which are explicitly devoted to heterogeneous doping and its dependence on external factors such as temperature, pressure, etc. in ion conducting oxides. A fundamental understanding of heterogeneous doping in oxides is essential to improve their functional properties beyond what can be achieved through homogeneous doping. In this work, we explore the defect chemistry and potential for job-sharing mechanisms through heterogeneous doping at interfaces in a model system of oxides with complex defect structures; acceptor-doped $SrTiO_3$ and $BaZrO_3$. These materials have been chosen due to the similarity in their defect structure and differences in their chemistry. While $BaZrO_3$ is a state-of-the-art proton conductor where the positive defects are mainly protons at low temperature and oxygen vacancies at high temperature, $SrTiO_3$ is dominated by oxygen vacancies at all practical temperatures and is widely used as a model material in the field of solid-state ionics.

2. Theoretical approaches and methodology

2.1 DFT calculations

All calculations were performed with plane-wave DFT as implemented in the VASP code²⁶⁻²⁸ using the GGA-PBE²⁹ and GGA-PBE+U functionals to describe the exchange-correlation part of the electronic energy in $BaZrO_3$ and $SrTiO_3$, respectively. A U-parameter of 4 eV, applied to the Ti *d*-states according to the approach introduced by Dudarev *et al.*³⁰, has been determined according to the method presented in reference³¹. However, the results are merely unaffected by the choice of U-parameter; for instance applying a U-parameter of 3 eV, affects the formation energy of defects by less than 50 meV. Projector augmented wave (PAW) potentials³²⁻³³ having the valence configurations $4s^2 4p^6 5s^2$, $5s^2 5p^6 6s^2$, $3s^2 3p^6 3d^2 4s^2$, $4s^2 4p^6 4d^2 5s^2$ and $2s^2 2p^4$ for Sr, Ba, Ti, Zr and O, respectively, were used. The calculations were performed with constant cut-off energy of 500 eV and ionic and electronic convergence criteria of 10^{-4} and 10^{-8} eV, respectively. Calculations on defects were performed with $3 \times 3 \times 3$ and $2 \times 2 \times 2$ supercells of cubic ($Pm\bar{3}m$) $BaZrO_3$ and tetragonal ($I4/mcm$) $SrTiO_3$, respectively. The Monkhorst-Pack scheme was used to sample the k-meshes of $2 \times 2 \times 2$ and $3 \times 3 \times 2$, which were found to yield sufficient convergence (within a few meV) of the total energies. For alignment of the defect energy levels (see details below), supercells of $1 \times 1 \times 11$

and $1 \times 1 \times 6$, with a corresponding $\mathbf{k}$ -mesh of $6 \times 6 \times 1$, were used. Surface calculations were performed with 11 and 13 layers of BaZrO_3 and SrTiO_3 , respectively. To calculate the vibrational formation entropies and zero point energies of defects, we performed phonon calculations according to the finite displacement method (with displacements of ± 0.01 Å) as implemented in the phonopy code.³⁴ The phonons were evaluated at the Γ -point, only.

2.2 Bulk thermodynamics

The free energy of defect formation is calculated according to

$$\Delta_f G_{\text{def}} = E_{\text{def}}^{\text{el}} - E_{\text{bulk}}^{\text{el}} + \Delta_f G_{\text{def}}^{\text{vib}} - \sum_i \Delta n_i \mu_i(T, p) + q(\varepsilon_F + \Delta\varepsilon), \quad (3)$$

where $E_{\text{def}}^{\text{el}}$ and $E_{\text{bulk}}^{\text{el}}$ are the total energy of a defect and a perfect supercell, respectively, and $\Delta_f G_{\text{def}}^{\text{vib}}$ is the vibrational free energy contribution to the formation energy. Δn_i is the change in the number of atom type i and μ_i is the corresponding chemical potential. q and ε_F are the effective charge of the defect and Fermi level, respectively. $\Delta\varepsilon$ compensates for the shift in band edges due to the jellium background for charged defects, and is calculated from the difference in electrostatic potential of atoms in the defective supercell and the perfect supercell far from the defect. The chemical potentials of gaseous species are obtained from:

$$\mu_i = \mu_i^\circ + E_i^{\text{ZP}} + H_i^\circ(T) - TS_i^\circ(T) + k_B T \ln\left(\frac{p_i}{p^\circ}\right), \quad (4)$$

where μ_i° is the standard chemical potential of gas molecule i . Due to poor description of small molecules in standard DFT, we calculated it from the energy of the separated atoms as obtained from DFT calculations, and experimental binding energies:

$$\mu_i^\circ = \sum E^{\text{atom,DFT}} + E^{\text{binding,exp}}. \quad (5)$$

E_i^{ZP} is the zero point energy and $H_i^\circ(T)$ and $S_i^\circ(T)$ are the standard enthalpy and entropy, respectively. The first is obtained from experimental vibrational spectroscopy, while the latter two are obtained from thermodynamic tables. The defect concentration is related to the formation Gibbs energy through:

$$\frac{c_i}{c_s - c_i - c_d} = \exp\left(-\frac{\Delta_f G}{k_B T}\right). \quad (6)$$

Here, c_i is the concentration of defect i that forms on lattice site s with concentration c_s . c_d is the concentration of all defects, other than i , that form on lattice site s . Site balance has been accounted for by:

$$\sum_i [i_{\text{O}}] + [\text{O}_0^\times] = 3. \quad (7)$$

Here, i runs on all defects that form on the oxygen site.

2.3 Segregation energies

The large lattice mismatch between SrTiO_3 and BaZrO_3 results in a heavily strained interface between these two materials causing DFT calculations to fail in describing the present system in the sense that a supercell containing both materials would have tilting of oxygen octahedra and consequently incorrect segregation energies. To avoid computational artefacts, we calculate the standard segregation energies of defects, *i.e.* the bulk-to-bulk segregation energies. This is done by calculating the defect formation energies with respect to the valence band maximum (VBM) after aligning it with respect to the vacuum level, which represents a global reference. Thus, the formation energies used to compare the stability and calculate the segregation energy of a defect is

$$\Delta_f G_{\text{def}} = E_{\text{def}}^{\text{el}} - E_{\text{bulk}}^{\text{el}} + \Delta_f G_{\text{def}}^{\text{vib}} - \sum_i \Delta n_i \mu_i(T, p) + q(\varepsilon_{\text{VBM,aligned}} + \Delta\varepsilon). \quad (8)$$

The main difference between this equation and Eq. (3), is the replacement of ε_F with $\varepsilon_{\text{VBM,aligned}}$. The calculations can also be performed by including the valence band offset, $\Delta\varepsilon_{\text{VBM}}$, with respect to one of the two materials, for instance BaZrO_3 (as we have done in this work) in Eq. (3), which becomes

$$\Delta_f G_{\text{def}} = E_{\text{def}}^{\text{el}} - E_{\text{bulk}}^{\text{el}} + \Delta_f G_{\text{def}}^{\text{vib}} - \sum_i \Delta n_i \mu_i(T, p) + q(\varepsilon_F + \Delta\varepsilon + \Delta\varepsilon_{\text{VBM}}). \quad (9)$$

The standard defect segregation energy is, as such, given by

$$\mu_{i,\text{seg}}^\circ = \mu_i^\circ - \mu_i^{\circ'} = \Delta_f G_{\text{def}} - \Delta_f G'_{\text{def}}, \quad (10)$$

where the prime denotes a different phase.

Fig. 1 shows a schematic representation of the alignment of the VBM in BaZrO_3 and the VBM offset between BaZrO_3 and SrTiO_3 . The latter is given by the difference in the ionization potential, IP, between the two materials,

$$\Delta\varepsilon_{\text{VBM}} = IP - IP', \quad (11)$$

which for the current system is 0.40 V (wrt. BaZrO_3) as shown in **Fig. 1a**. To determine the IP, DFT calculations on slabs of BaZrO_3 and SrTiO_3 are necessary. Although the IP can be obtained from a single DFT calculation, the presence of band bending and electronic states at the surface makes it challenging to determine the actual VBM position in the slab calculation. Therefore, we use the VBM from a bulk calculation such that

$$IP = U_{\text{vac}} - \varepsilon_{\text{VBM}} = U_{\text{vac.slabs}} + U_{\text{diff}} - \varepsilon_{\text{VBM}}, \quad (12)$$

where U_{vac} is the potential of vacuum with respect to bulk and $U_{\text{diff}} = U_{\text{bulk}} - U_{\text{slab}}$, is the difference in the average electrostatic potential of the bulk region in the slab and bulk calculations, as illustrated in **Fig. 1b**. The actual potentials are shown in **Fig. 2**.

Fig. 1. A schematic representation of the alignment of (a) VBM between BaZrO₃ and SrTiO₃ and (b) band structure of BaZrO₃ wrt. vacuum level to determine the ionization potential, IP . Figure (b) is not at scale.

Fig. 2. The average electrostatic potential in bulk and a slab of BaZrO₃ and their difference.

Our method for evaluation of segregation energies is computationally feasible as it avoids the explicit treatment of the interface system, thus allowing high throughput screening. Neglect of segregation to the interfacial plane itself can for this system be justified by the structural and chemical similarity of the two phases, and we expect the formation energy of defects at epitaxial interfaces to fall within the range of the two bulk phases (as opposed to in *e.g.* bulk/grain boundary or bulk/surface system). For more chemically and structurally different interfaces, such as heterointerfaces with inherent charge imbalance (*e.g.* $A^{2+}B^{4+}O_3/A^{3+}B^{3+}O_3$), defect segregation to the interface plane(s) should be explicitly included. Furthermore, it should be mentioned that although the GGA-PBE(+U) exchange correlation functional significantly underestimates the bandgap of perovskite oxides compared to hybrid functionals,³⁵⁻³⁶ the defect segregation energies are not affected since the alignment of band edges we perform yields the same relative band edge positions as in a supercell containing both materials.

2.4 Space-charge thermodynamics

We apply the widely adopted abrupt model to describe the interface, *i.e.* we assume that the defect formation energies and the atomic structure in the space-charge region is the same as in the bulk materials and that these properties change abruptly across the interface plane. As such, the electrochemical potential of species i , $\tilde{\mu}_i$, within one material can be written as

$$\tilde{\mu}_i = \mu_i^\circ + k_B T \ln \left(\frac{c_i(x)}{c_s - c_i(x)} \right) + q_i \varphi(x), \quad (13)$$

where $\varphi(x)$ is the electrostatic potential at a distance x from the interface (note that $x = \infty$ corresponds to bulk, where $\varphi = 0$). At equilibrium, the electrochemical potential becomes constant throughout the interface, such that:

$$\mu_i^\circ + k_B T \ln \left(\frac{c_i(x)}{c_s - c_d(x) - c_i(x)} \right) + q_i \varphi(x) = \mu_i^{\circ'} + k_B T \ln \left(\frac{c'_i(x')}{c'_s - c'_d(x') - c'_i(x')} \right) + q_i \varphi(x'), \quad (14)$$

where the prime denotes that the defect resides in the adjacent phase or at a different position within the same phase (then $\mu_i^{\circ'} = \mu_i^\circ$). Rearranging Eq. (14) and setting $x' = +\infty$ gives the concentration of defects as a function of bulk concentrations and the electrostatic potential with respect to that in bulk, $\Delta\varphi(x) = \varphi(x) - \varphi_{bulk}$:

$$c_i(x) = \frac{(c_s - c_d(x))c'_{i,bulk} \exp \left(\frac{\mu_i^{\circ'} - \mu_i^\circ}{k_B T} + \frac{q_i(\varphi(x') - \varphi(x))}{k_B T} \right)}{c'_s - c'_{i,bulk} - c'_{d,bulk} - c'_{i,bulk} \exp \left(\frac{\mu_i^{\circ'} - \mu_i^\circ}{k_B T} + \frac{q_i(\varphi(x') - \varphi(x))}{k_B T} \right)}, \quad (15)$$

where $c'_s = c_s$ when x is in the reference material. If the electrostatic potential at the interface ($\phi = \Delta\varphi(x = 0)$) is known, then the potential as a function of distance can be determined from Poisson's equation,

$$\frac{d^2}{dx^2} \Delta\varphi(x) = -\frac{\rho(x)}{\epsilon}, \quad (16)$$

which relates the charge density, $\rho(x)$, to the electrostatic potential. ϵ is the dielectric constant. The charge density is given by

$$\rho(x) = \sum_i e q_i c_i(x). \quad (17)$$

Although ϕ and ϕ' are unknown, the total electrostatic potential difference across the interface, Φ , is known. Rearranging Eq. (14) and setting $x = -\infty$ and $x' = +\infty$ give Φ in terms of the segregation energies, $\mu_{i,seg}^\circ = \mu_i^{\circ'} - \mu_i^\circ$, and bulk concentrations of defects:

$$\Phi = \phi - \phi' = \frac{1}{q_i} \left[(\mu_{i,seg}^\circ) + k_B T \ln \left(\frac{c'_{i,bulk} [c_s - c_{i,bulk}]}{c_{i,bulk} [c'_s - c'_{i,bulk}]} \right) \right]. \quad (18)$$

Solving this set of equations numerically with appropriate boundary conditions gives the spatial electrostatic potential and concentration profiles.

The required boundary conditions are constant electrostatic potential in bulk,

$$\frac{d}{dx} \varphi(x) = 0 \Big|_{x=\infty}, \quad (19)$$

and, in absence of charge accumulation at the interface plane, constant dielectric function at the interface,

$$\varepsilon \frac{d}{dx} \varphi(x) = -\varepsilon' \frac{d}{dx'} \varphi(x') \Big|_{x=x'=0}, \quad (20)$$

which ensures charge neutrality in the system.

3. Results and discussion

Two defects are included in this work; oxygen vacancies, $v_{\text{O}}^{\bullet\bullet}$, and protons, $\text{OH}_{\text{O}}^{\bullet}$. Although electron holes dominate the electrical conductivity in BaZrO_3 and SrTiO_3 at high temperatures and oxygen partial pressures, they have been omitted due to their low concentration. The relative concentrations of $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$ in SrTiO_3 and BaZrO_3 are determined by the hydration enthalpies, which are calculated to -0.84 and -0.39 eV, respectively, in line with previous computational and experimental works.³⁷⁻³⁹ Including vibrational effects (*i.e.*, ZPEs and entropies) for the defects and gaseous species increases the enthalpies somewhat to -0.81 and -0.29 eV. Although these differ slightly from the experimental enthalpies, it will not affect our analysis significantly. Thus, BaZrO_3 will be predominated by protons below 600 K, above which the concentration of $v_{\text{O}}^{\bullet\bullet}$ becomes significant, as shown in **Fig. 3b**. On the other hand, SrTiO_3 starts to lose $\text{OH}_{\text{O}}^{\bullet}$ already at 150 K, and becomes completely predominated by oxygen vacancies above 200 K, **Fig. 3a**. SrTiO_3 will as such never be dominated by protons under realistic conditions. However, it is still of interest as a model material since it exhibits a transition from a $\text{OH}_{\text{O}}^{\bullet}$ to a $v_{\text{O}}^{\bullet\bullet}$ dominated defect structure under conditions where the counter-phase (here BaZrO_3) remains dominated by $\text{OH}_{\text{O}}^{\bullet}$, allowing evaluation of the implications of hydration/dehydration of both phases on the heterogeneous doping effect.

Fig. 3. Defect concentrations in bulk acceptor doped (10 mole %) SrTiO₃ (a) and BaZrO₃ (b) as a function of inverse temperature in wet ($p_{\text{H}_2\text{O}} = 0.03$ atm) oxygen.

In the defect chemistry of interfaces, an essential parameter is the defect segregation enthalpy, ΔH_{seg} , which is a measure of the relative stability of defects in the two phases. ΔH_{seg} is usually calculated from the defect formation energies in bulk-like layers of a supercell containing slabs of two materials. In the BaZrO₃/SrTiO₃ system, which exhibits relatively large lattice mismatch ($\sim 7\%$),⁴⁰ DFT fails in predicting the correct interface structure, thus resulting in unphysical structural distortion, and consequently inaccurate defect energetics. To circumvent this artefact, we, initially, calculate and use standard segregation enthalpies, *i.e.* bulk-to-bulk segregation energies. The role of strain will be addressed explicitly towards the end of this section. Furthermore, defect segregation to the interface plane is negligible compared to the bulk-to-bulk segregation energy in epitaxial thin films of materials having the same structure, and is therefore not included. The latter has been confirmed by calculations on other, similar perovskite interfaces.

According to our model, segregation of $v_{\text{O}}^{\bullet\bullet}$ from SrTiO₃ to BaZrO₃ according to

exhibits a strongly negative enthalpy of -0.64 at 0 K, which may arise from the more basic character of BaZrO₃ than SrTiO₃. The segregation enthalpy of $\text{OH}_{\text{O}}^{\bullet}$ to BaZrO₃, on the other hand, is somewhat weaker, -0.56 eV. The segregation energies of the two defects are coupled through the bulk hydration enthalpies, and can be expressed as

$$\Delta H_{\text{OH}_{\text{O}}^{\bullet}}^{\text{seg}} = \frac{\Delta H_{v_{\text{O}}^{\bullet\bullet}}^{\text{seg}} + \Delta(\Delta H_{\text{hydr}})}{2}. \quad (22)$$

This equation shows that $\Delta H_{\text{OH}_{\text{O}}^{\bullet}}^{\text{seg}}$ can even be positive if materials with a large enough difference in ΔH_{hydr} are chosen. Moreover, if one segregation enthalpy is known, then segregation enthalpies of all other defects that can be related through a defect reaction can be determined from, for instance experimental, reaction enthalpies.

The electrostatic potential, Φ , that arises from defect segregation across the interface is directly coupled to the segregation enthalpies (Eq. (18)). In the limit where both materials are dominated by $v_{\text{O}}^{\bullet\bullet}$ or $\text{OH}_{\text{O}}^{\bullet}$, Φ is -0.32 or -0.56 V, respectively, at 0 K. The temperature dependence of Φ is shown in **Fig. 4**. The red curve shows the electrostatic potential that arises from $v_{\text{O}}^{\bullet\bullet}$ segregation, *i.e.* in the limit where reaction Eq. (21) dominates. In that limit, Φ exhibits a strong, positive temperature dependence and eventually exceeds 0.0 V at 1550 K. This curve is valid under dry conditions and/or high temperature. Under such conditions, the temperature dependence of Φ is given by the vibrational segregation entropy, under the assumption that the parent materials have the same doping level such that the configurational term in Eq. (18) cancels. For the current system, the segregation entropies are -40 J/mol K for $v_{\text{O}}^{\bullet\bullet}$ and 10 J/mol K for $\text{OH}_{\text{O}}^{\bullet}$. Interestingly, the negative segregation entropy of $v_{\text{O}}^{\bullet\bullet}$ suppresses defect segregation to BaZrO_3 , hence the positive temperature dependence and inversion of Φ at high temperature, which eventually causes defects to segregate to SrTiO_3 . At lower temperatures, where $\text{OH}_{\text{O}}^{\bullet}$ is the dominating defect, Φ is increasingly negative with increasing temperature as a result of the positive segregation entropy of $\text{OH}_{\text{O}}^{\bullet}$, which contributes to increased defect segregation to BaZrO_3 . Thus, this example illustrates how materials can be chosen in order to tune the defect chemical properties of interfaces based on knowledge of their thermodynamics.

Fig. 4. The electrostatic potential across the interface between SrTiO_3 and BaZrO_3 as a function of temperature. The red and blue curves show the potential if both materials contain only $v_{\text{O}}^{\bullet\bullet}$ or $\text{OH}_{\text{O}}^{\bullet}$, respectively. The black curve shows the development of the potential when both defects are included.

The defect structure is rarely dominated by a single defect, and in SrTiO_3 and BaZrO_3 , the presence of $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$ results in three distinct defect situations at low, intermediate and high temperatures. At high and low temperatures, the materials are dominated by $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, respectively, and the electrostatic potential difference between the two bulk phases is described according to the discussion in the previous paragraph. At intermediate temperatures, SrTiO_3 is dominated by $v_{\text{O}}^{\bullet\bullet}$, with $\text{OH}_{\text{O}}^{\bullet}$ as minority defect, while BaZrO_3 is dominated by $\text{OH}_{\text{O}}^{\bullet}$, with $v_{\text{O}}^{\bullet\bullet}$ as minority defect. In this region, both defects contribute to Φ through the second term on the right hand side of Eq. (18), which becomes substantial due to the large difference in the chemical activity of defects in the two

materials. The black curve in **Fig. 4** shows the potential when both $v_O^{\bullet\bullet}$ and $OH_O^\bullet$ are included in the calculation. In the transition region, the potential takes on values in between the two extremes, where either $v_O^{\bullet\bullet}$ or $OH_O^\bullet$ dominates. The dependence of Φ on the defect concentration in the constituting materials reflects that it is strongly affected by changes in external parameters such as doping type/level and atmospheric conditions. For instance, reducing p_{H_2O} at constant temperature would result in shifting the transition region in **Fig. 4** to the left and consequently increasing the potential, which would affect the defect chemistry and conductivity as discussed below.

In all three limiting cases, $v_O^{\bullet\bullet}$ and $OH_O^\bullet$ accumulate on the $BaZrO_3$ side of the interface due to their high chemical potential in $SrTiO_3$. Thus, $BaZrO_3$ acts as a donor phase, while $SrTiO_3$, effectively, acts as an acceptor, in conjunction with each other. The situation is the opposite of that at a grain boundary in $BaZrO_3$, which acts as a structural donor dopant due to the positively charged core. Consequently, with respect to the bulk materials, the electrostatic potential arising from defect segregation becomes negative in $BaZrO_3$ and positive in $SrTiO_3$. Examples of the concentration and electrostatic potential profiles at 150, 600 and 1200 K in wet O_2 are shown in **Fig. 5**. These profiles have been calculated according to the Mott-Schottky model, where cations are assumed to be immobile, which represents the defect situation in samples made at low temperature, for instance by PLD. Towards the interface, the concentration of $v_O^{\bullet\bullet}$ and $OH_O^\bullet$ increase in $BaZrO_3$ and significantly decrease in $SrTiO_3$. In both materials, the enrichment/depletion effect is stronger for $v_O^{\bullet\bullet}$ than for $OH_O^\bullet$, due to the charge difference of the two species. Except for the first 1-3 nm from the boundary, which corresponds to the extent of the space-charge layer, the defect concentrations and other parameters are expected to be as in the bulk phases. For $SrTiO_3$, the space-charge layer is wider compared to $BaZrO_3$, which stems from its higher dielectric constant and the limited number of defects that can be depleted. In $BaZrO_3$, availability of many regular lattice sites where defects can form results in a narrower space-charge layer. The resulting space-charge layer width and concentration profiles in $SrTiO_3$ at 600 K are very similar to those calculated for grain boundaries⁴¹. As **Fig. 5** shows, the space-charge layer width decreases with increasing temperature, at the same time the concentration enrichment (depletion) is suppressed. This is a consequence of the thermal energy that balances the segregation enthalpy and the increase of Φ (*i.e.* smaller absolute value).

Fig. 5. The concentration profiles of defects as a function of distance from the interface at 150 (a), 600 (b) and 1200 K in wet ($p_{H_2O} = 0.03$ atm) oxygen.

Fig. 5b shows an important aspect of the difference in the defect structure of BaZrO₃ and SrTiO₃ that is encountered at intermediate temperatures where mass balance cannot be achieved within the isolated composite system as SrTiO₃ and BaZrO₃ are dominated by $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, respectively. Under such conditions, depletion of $v_{\text{O}}^{\bullet\bullet}$ in SrTiO₃ involves incorporation of O^{2-} that cannot be provided by BaZrO₃, at the same time SrTiO₃ cannot provide the $\text{OH}_{\text{O}}^{\bullet}$ that are enriched in BaZrO₃. Consequently, the surroundings are involved through a heterogeneous reaction where a job-sharing process results in incorporation of water when the two materials come into contact with each other. The same applies upon a change in Φ , for instance due to a change in temperature, in a system where the materials already are in contact with each other. In that respect, the process corresponds to reversible job-sharing storage of H₂O upon temperature cycling. Job-sharing mechanisms can as such be utilized to enhance the proton concentration through heterogeneous doping and thereby the conductivity. This can be achieved by choosing materials in which segregation of defects to, for instance, BaZrO₃ has negative enthalpy and strongly positive entropy such that in addition to enrichment of protons, dehydration of nanocomposites of BaZrO₃ is limited at high temperature. Even though BaZrO₃ still dehydrates with increasing temperature, increasingly negative Φ would result in more vacancies in the space-charge layer and therefore shift the hydration reaction to the right such that the overall proton concentration may become constant or even increase with increasing temperature.

Fig. 6 compares the defect concentration and electrostatic potential profiles calculated according to the Mott-Schottky and Gouy-Chapman models. The latter represents the situation in samples quenched from high temperatures. Therefore, the dopant concentration profile has been fixed to that at 1200 K – under which the concentration of dopant can be considered as frozen-in. The accumulation of dopants in SrTiO₃ results in enhanced concentration of $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$ and reduced space-charge layer width, compared to the Mott-Schottky model. This is in line with experimental observations near grain boundaries of SrTiO₃ and BaZrO₃, where dopant accumulation has been confirmed by high-resolution microscopy/spectroscopy methods⁴²⁻⁴³. Similarly, the depletion of dopant is supposed to reduce the defect enrichment in BaZrO₃; however, that is not the case – in fact, the Gouy-Chapman model predicts that the concentration of $\text{OH}_{\text{O}}^{\bullet}$ in the space-charge layer is higher than predicted by the Mott-Schottky model, 0.44 vs. 0.41 C/m². This stems from the accumulation of acceptors in SrTiO₃, which is three times as high as the dopant depletion in BaZrO₃, and thus more than cancels its effect. Therefore, compared to grain boundaries and surfaces, equilibration of dopants at a heterogeneous interface has less influence on the concentration of defects in the space-charge zone.

Fig. 6. The concentration profiles of defects as a function of distance from the interface at 300 K in wet ($p_{\text{H}_2\text{O}} = 0.03$ atm) oxygen, as calculated according to the Mott-Schottky (a) and Gouy-Chapman model (b).

So far the effect of strain on the physicochemical properties of the interface has not been considered. Strain may, however, affect both the dielectric constant and the formation energy of defects in the near-interface region of both materials. While changes in the dielectric constant have minor effects on the spatial distribution of defects in the near-interface space-charge zone, the integrated concentration practically remains unaffected. In contrast, the change in the defect formation energy may be more important. In general, compressive strain stabilizes defects that exhibit negative formation volume – such as $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, where the formation volumes are -18 and $-4 \text{ \AA}^3$, respectively⁴⁴ – while tensile strain stabilizes defects that exhibit positive formation volume. In addition, the shape of a defect may also be instrumental. For an epitaxial (0 0 1) terminated $\text{BaZrO}_3/\text{SrTiO}_3$ interface, the average strain is 3 %. Calculations on bulk BaZrO_3 and SrTiO_3 subjected to 3 % compressive and tensile strain in the a-b plane changes the formation energy of $v_{\text{O}}^{\bullet\bullet}$ by -0.42 and 0.19 eV, respectively. For $\text{OH}_{\text{O}}^{\bullet}$, the corresponding changes are 0.27 and 0.05 eV, respectively. Although these numbers are significant, they represent an upper limit as formation of dislocations may moderate the strain to some extent. The change in formation energy (and defect affinity) as a function of strain in BaZrO_3 and SrTiO_3 are presented in **Fig. 7**. For $\text{OH}_{\text{O}}^{\bullet}$ in BaZrO_3 , the effect of strain on the formation energy is opposite to that of $v_{\text{O}}^{\bullet\bullet}$ despite its negative formation volume. This may be a result of the shape of the two defects; while $\text{OH}_{\text{O}}^{\bullet}$ gives an anisotropic distortion of the lattice, $v_{\text{O}}^{\bullet\bullet}$ gives tetragonal distortion. For the current interface with average compressive and tensile strain of 3 % in BaZrO_3 and SrTiO_3 , the segregation energies become -1.71 and -0.60 eV for $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, respectively.

Fig. 8 shows the electrostatic potential and defect concentration profiles across the interface by accounting for strain. Indeed, due to larger electrostatic potential difference, more defects are enriched (depleted) in the two materials, and the spatial extent of the space-charge layer is increased. At 600 and 1200 K, the concentration of $v_{\text{O}}^{\bullet\bullet}$ in the space-charge region of BaZrO_3 becomes significant, approaching unity. Likewise, the concentration of $\text{OH}_{\text{O}}^{\bullet}$ increases towards the interface, before it starts to flatten out and eventually decrease close to the phase boundary. This behavior stems from the competition between $v_{\text{O}}^{\bullet\bullet}$ and $\text{OH}_{\text{O}}^{\bullet}$, both of which form on the O-sublattice.

Fig. 7. Change in the formation energy of defects (relative to the unstrained material) as a function of strain in BaZrO₃ (a) and SrTiO₃ (b). The solid lines show the change in formation energy – the dashed lines also include alignment with respect to the vacuum level (*i.e.* represent the change in defect affinity). Notice the difference in scale.

Fig. 8. The concentration profiles of defects as a function of distance from the interface at 150 (a), 600 (b) and 1200 K in wet ($p_{\text{H}_2\text{O}} = 0.03$ atm) oxygen.

These results show that the total concentration of protons at heterointerfaces and in nanocomposites can far exceed those of the parent bulk phases which in turn can enhance the in-plane proton transport properties of for instance multi-layered nanostructured films. This also demonstrate that the macroscopic properties of multilayered thin films differ significantly from those of the bulk materials. For instance, the electrical conductivity of SrTiO₃/BaZrO₃ films is expected to be dominated by the high electron hole conductivity of SrTiO₃, which in the bulk material is proportional to $p_{\text{O}_2}^{1/4}$ and has no dependence on $p_{\text{H}_2\text{O}}$. However, in a nanostructured, multilayered thin film with a proton conductor, where the volumetric concentration of interfaces is significant, a change in $p_{\text{H}_2\text{O}}$ brings about a change in Φ , as shown in **Fig. 4**, which in turn affects the hole concentration in the space-charge layer, and consequently, the macroscopic conductivity.

4. Conclusions

First principles calculations reveal that SrTiO₃/BaZrO₃ nanostructures may lead to heterogeneous doping that strongly affects the defect chemical and transport properties of the two materials. Both $v_O^{\bullet\bullet}$ and $OH_O^\bullet$ exhibit negative segregation enthalpies of -0.64 and -0.56 eV, respectively, from SrTiO₃ to BaZrO₃, resulting in depletion of defects in SrTiO₃ and enrichment in BaZrO₃. Effectively, this corresponds to acceptor doping of BaZrO₃ and donor doping of SrTiO₃. At intermediate temperatures, reversible incorporation of H₂O occurs upon change in the electrostatic potential, which exhibits a strong temperature dependence that is determined by the segregation entropy of the two defects. Such job-sharing mass exchange may allow storage of H₂ in nanocomposites of proton conductors and electron conductors, such as metals or for instance donor-doped SrTiO₃. Furthermore, the total concentration of $OH_O^\bullet$ in nanostructured heterostructures and composites of BaZrO₃ and SrTiO₃ is significantly higher than in the bulk materials, suggesting that their ionic conductivity will be higher than in the individual phases since protons exhibit higher diffusivity than oxygen vacancies. Finally, strain may substantially affect the segregation energies of defects and may as such, together with homogeneous doping, be used to tailor the properties of interfaces. In conclusion, our results demonstrate how appropriate choice of materials with different physiochemical properties may enable heterogeneous doping in nanocomposites, yielding materials that are no longer subjected to the local electroneutrality constraints of the bulk materials.

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