Segregation and trapping of oxygen vacancies near the SrTiO₃ Σ 3 (112) [$\bar{1}$ 10] tilt grain boundary

Bin Liu¹, Valentino R. Cooper^{1,*}, Yanwen Zhang^{1,2}, and William J. Weber^{2,1,*}

¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge,
Tennessee 37831, USA

²Department of Materials Science and Engineering, University of Tennessee, Knoxville,
Tennessee 37996, USA

*Corresponding Author:

Valentino R. Cooper

Materials Science and Technology Division

Oak Ridge National Laboratory

Oak Ridge, TN 37831

Phone: 1-865-574-5164

E-mail: coopervr@ornl.gov

W.J. Weber

Department of Materials Science and Engineering

University of Tennessee

Knoxville, TN 37996

Tel: +1-865-974-0415

Email: wjweber@utk.edu

Abstract

In nanocrystalline materials, structural discontinuities at grain boundaries (GBs) and the segregation of point defects to these GBs play a key role in defining the structural stability of a material as well as its macroscopic electrical/mechanical properties. In this study, the segregation of oxygen vacancies near the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB in SrTiO_3 is explored using density functional theory. We find that oxygen vacancies segregate towards the GB, preferring to reside within the next nearest neighbor layer. This oxygen vacancy segregation is found to be crucial for stabilizing this tilt GB. Furthermore, we find that the migration barriers of oxygen vacancies diffusing towards the first nearest-neighbor layer of the GB are low, while those away from this layer are very high. The segregation and trapping of the oxygen vacancies in the first nearest-neighbor layer of GBs are attributed to the large local distortions, which can now accommodate the preferred six-fold coordination of Ti. These results suggest that the electronic, transport, and capacitive properties of SrTiO_3 can be engineered through the control of GB structure and grain size or layer thickness.

KEYWORDS: SrTiO_3 , grain boundary, density functional theory, oxygen vacancy

1. Introduction

Nanostructured ceramic-oxides, which often exhibit enhanced properties compared to their microcrystalline counterparts, have attracted increasing attention in recent years. At grain boundaries (GBs), structural discontinuities result in specific GB structures, as well as the segregation of intrinsic point defects and dopants away from or towards such GBs. These features often strongly affect the macroscopic electrical and mechanical properties of a material and thus become more significant in nano-crystalline materials [1-3]. For instance, the special nonlinear I - V characteristics observed in Nb-doped SrTiO_3 bicrystals are linked to the segregation of strontium vacancies to the GB [4]. Therefore, understanding the effects of defects near GBs on physical and chemical properties is fundamental for optimizing a material through nano-structuring. Recent studies have demonstrated that it is possible to create, manipulate and analyze point defects in bulk oxides [5-7]; however, the engineering of GBs and their associated defects in oxides is still not well advanced or understood.

SrTiO_3 is an ideal model system, due to both its simple cubic symmetry and its wide range of applications, including insulating layers in dynamic random-access memories, [8] ferroelectric thin-film structures, [9] multilayer ceramic capacitors, [10] high- T_c superconductor devices, [11] potential gate oxide candidates, [12] and the immobilization of high-level nuclear wastes [13]. Additionally, oxygen vacancies (V_O), which form readily within SrTiO_3 , have been shown to be the driving force behind the blue and green light emission [14-15] and the high n -type conductivity [16-17]. While, the energetics of oxygen vacancies and their effects on the properties of bulk SrTiO_3 are understood, less is known about their energetics at GBs. In particular, the effects of atomic scale oxygen nonstoichiometry at GBs are poorly understood.

This is partly due to the difficulty in directly observing oxygen atoms, which demands rather dedicated techniques such as high-voltage electron microscopy [18,19] and aberration corrected transmission electron microscopy (TEM) with a negative spherical aberration correction [20, 21]. First principles calculations, however, have been successfully used to categorize the three-dimensional GB structures in SrTiO_3 [22-24]. It has been demonstrated that these GBs are intrinsically nonstoichiometric [23-24]. Such nonstoichiometry is dominated by various types of point defects at different GBs, which further leads to structural distortions and significant changes in material properties [23-24]. As the most important point defect, the migration/trapping of oxygen vacancies across and at GBs is expected to be critical in defining the electronic, transport, and capacitive properties of SrTiO_3 . The ability to tailor the oxygen vacancy content at GBs may be the key to understanding, manipulating and realizing the full functionality of SrTiO_3 .

In this work, the segregation and diffusion of oxygen vacancies as a function of distance away from the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB of SrTiO_3 are studied using density functional theory (DFT). It is found that oxygen vacancies segregate towards the GB, preferring to reside within its nearest neighbor layer. The migration barriers of oxygen vacancies diffusing to the first nearest-neighbor layer of the GB are low, while those away from this layer are very high. The segregation and trapping of the oxygen vacancies in the first nearest-neighbor layer of the GBs are attributed to the large local distortion which achieves the preferred six-fold coordination of Ti. Furthermore, the V_O segregation in the vicinity of this GB, especially in the first nearest neighbor layer, is crucial to GB stability. Based on these results, the tailoring of electronic, transport, and capacitive properties of SrTiO_3 by controlling GB structure and grain size or layer thickness may

be achieved.

2. Calculation details

All density functional theory (DFT) calculations were performed with the Vienna Ab-Initio Simulation Package (v.5.2.12) code using the projector augmented wave (PAW) method [25]. The generalized gradient approximation with the exchange-correlation functional of Perdew-Burke-Ernzerhof (GGA-PBE) was used [26]. To correct the on-site Coulomb interaction of the $3d$ orbitals, a rotationally invariant $+U$ method [27] was applied with $U = 5.0$ eV and $J = 0.64$ eV [28]. This approach has been proven to be effective for studying oxygen vacancies in SrTiO_3 and to produce the localized in-gap states present in the material [15, 28]. All computations were performed with a $4 \times 2 \times 1$ Monkhorst-Pack k-point sampling [29] and a cutoff energy of 400 eV for the plane wave basis set. The crystal structures were relaxed until the forces on individual atoms were smaller than 0.02 eV/Å. Spin polarization was taken into account in all calculations. The calculated lattice constant of 3.93 Å, is in typical DFT agreement with the experimental measurement of $a_0 = 3.89$ Å [30]. Diffusion paths and migration barriers of oxygen vacancies were investigated by the climbing-image nudged elastic band (CI-NEB) method [31].

The mirror-symmetric $\text{SrTiO}_3 \Sigma 3$ (112) $[110]$ tilt GB, created based on knowledge from both theoretical and experimental results [23], is depicted in Fig. 1. This GB is comprised of alternating O_2 and SrTiO planes. Our supercell has the dimensions $(\sqrt{3}a_0, 2\sqrt{2}a_0, 3\sqrt{6}a_0)$ in the directions $([11\bar{1}], [\bar{1}10], [112])$ and consists of 180 atoms. The supercell size is validated using a larger supercell having the dimensions $(2\sqrt{3}a_0, 2\sqrt{2}a_0, 3\sqrt{6}a_0)$. In this cell, the defect formation energy of V_{O}^{2+} varies less than 0.01 eV, which indicates that image-defect interactions

and the effects of TiO_6 octahedra distortions due to a periodic array of vacancies are negligible. The calculated formation energy of the stoichiometric GB, which is the energy difference between the supercell with and without the GB, is $\sigma_{\text{GB}} = 1.08 \text{ J/m}^2$, in good agreement with the previous theoretical value, 1.07 J/m^2 [22].

The formation energy of V_O , E_f , was evaluated as [7, 32]

$$E_f = E_d - E_p + \sum n_i \mu_i + q(\Delta E_F + E_{\text{VBM}}) \quad (1)$$

where E_d and E_p are the total energies of supercells with and without a point defect, respectively, q is the charge state, n_i is the number of atoms being removed, and μ_i is the oxygen chemical potential. The oxygen chemical potential range (from -10.24 eV to -4.93 eV) was determined by the following thermodynamic limits: (1) the limit of SrTiO_3 stoichiometry, $\mu_{\text{Sr}} + \mu_{\text{Ti}} + 3\mu_{\text{O}} = \mu_{\text{SrTiO}_3}$; (2) the limit of the system against decomposition into its constituent elements, $\mu_{\text{Sr}} \leq \mu_{\text{Sr}}^{\text{bulk}}$, $\mu_{\text{Ti}} \leq \mu_{\text{Ti}}^{\text{bulk}}$ and $\mu_{\text{O}} \leq \mu_{\text{O}_2}^{\text{O}_2}$; and (3) the limit of either SrO or TiO_2 precipitating from bulk SrTiO_3 , $\mu_{\text{Sr}} + \mu_{\text{O}} \leq \mu_{\text{SrO}}$ and $\mu_{\text{Ti}} + 2\mu_{\text{O}} \leq \mu_{\text{TiO}_2}$. E_{VBM} and ΔE_F are the energy levels corresponding to the valance band maximum (VBM) and the Fermi level measured from the VBM, respectively. The Fermi level ΔE_F changes its position within the band gap, E_g , which is represented by the energy difference between the VBM and the conduction-band minimum (CBM) as $E_g = E_p(-1) + E_p(+1) - 2E_p(0)$. -1, +1 and 0 are the charge states of the supercell. The calculated band gap value E_g of 2.68 eV is smaller than the experimental one 3.25 eV [33]. This underestimation is a well-known DFT error and does not affect our main conclusions. The vacancy formation energies in the GB and the vicinity of the GB, E_f^{GB} , were determined as a function of the vacancy position as shown in Fig. 1. For reference, the vacancy formation energy in the bulk, E_f^{bulk} , was also determined. The segregation energy, E_{seg} , of V_O was

thus calculated as

$$E_{seg} = E_f^{GB} - E_f^{bulk} \quad (2)$$

Here, it is noted that the segregation energy provides the simplification of not having to consider the effects of both the oxygen chemical potential and the electron Fermi level.

The formation energy of the nonstoichiometric GB (E_f^{NGB}) was calculated by:

$$E_f^{NGB} = E_{NGB} - E_p + \sum n_i \mu_i + q(\Delta E_F + E_{VBM}) \quad (3)$$

Where, E_{NGB} is the supercell consisting the GB and one V_O . Since the segregation of an V_O to the vicinity of the GB and the concentration of V_O in the vicinity of GB are expected to be higher than in bulk, the bulk without V_O , E_p , was adopted as the reference.

3. Results and discussions

3.1 Segregation of oxygen vacancies

The calculated segregation energies for charged oxygen vacancies in the GB and its vicinity are shown in Fig. 2 (a). A significant segregation of V_O to layer 1 is observed for all charge states, with segregation energies of -2.01, -1.59 and -1.78 eV for V_O^0 , V_O^{1+} and V_O^{2+} , respectively. Similarly, the segregation energies of layers 2 to 4 are favorable (i.e. less than zero), suggesting the possible accumulation of a small amount of V_O in these layers. In contrast, the segregation energy for an V_O at the $SrTiO_3$ GBs (layer 0) is positive; indicating that the segregation of V_O to the GB is energetically unfavorable relative to the bulk. Layers 5 to 10 return to the bulk behavior.

The transition levels for the charge states of V_O as a function of electron Fermi level, E_F , is shown in Fig. 3. We observe a bulk-like region at the GB (layer 0) where $2+/1+$ and $1+/0$

transition levels occur at $E_F = 1.95$ eV and 2.30 eV, respectively. However, V_O s in layers 1 to 5 exhibit a negative U behavior, which is evident by a single $2+/0$ transition and the absence of the $2+/1+$ and $1+/0$ transitions. Again we observe that layers 6 to 10 return to bulk-like behavior with clearly defined $2+/1+$ and $1+/0$ transition levels. As such, these results demonstrate the significant influence of the GB on the electronic acceptor/donor levels of the oxygen vacancy, which may guide the control of the optical properties and conductivity in SrTiO_3 through engineering the density and type of GBs.

To better understand the origin of the segregation tendency of V_O s near the GB, we examine the effect of an V_O on GB stability and local structure. While previous studies have focused on the effects of point defects in the GB layer (i.e. layer 0) on the GB stability; [1,3] here, we examine the effects of an V_O both at the GB and in the neighboring layers. Fig. 4 depicts the grain boundary formation energy as a function of chemical potential and electron Fermi energy for an V_O in layers 0 and 1. Fig 4 (a) shows that a nonstoichiometric GB with an V_O at the GB has only a small region of stability, i.e. under oxygen poor conditions and low electron Fermi energies. Such strict conditions are expected to be difficult to achieve in experiments. Furthermore, a nonstoichiometric GB with either a neutral or $1+$ V_O in the GB layer is energetically unfavorable under all conditions. In contrast, an V_O in layer 1 significantly stabilizes the GB under a wide range of oxygen chemical potentials and electron Fermi levels, as shown in Fig. 4 (b). Here, the nonstoichiometric GB is dominated by V_O^{2+} and V_O^0 at low and high Fermi levels, respectively. A comparison with V_O in the GB layer indicates that there is a much lower formation energy for the nonstoichiometric GB with an V_O in layer 1, at the same oxygen chemical potential and Fermi level. Under the extreme condition of $\mu_O = -10.24$ eV and $\Delta E_F = 0$ eV, the GB formation energy decreases from 1.08 eV in the stoichiometric case to 0.41

eV in the nonstoichiometric case with an V_O in layer 1. An V_O in layers 2 to 4, also leads to a reduction in the GB formation energy, albeit not as dramatic as an V_O in layer 1. Nevertheless, such defect segregation near the GB should play a significant role in the stability of the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB observed in experiments.

The above trends with regards to V_O segregation energy and the effects on the stability of the GB can be readily understood through an analysis of the GB structure upon creation of an V_O . The pair distribution functions (PDF) for Ti-O six nearest neighbors for V_O^{2+} in the bulk and in layers 0 to 3 are shown in Fig. 5. The corresponding relaxed local configurations are shown as insets. In bulk cubic $SrTiO_3$, all Ti atoms are six-fold coordinated with oxygen, and its PDF only has a simple peak at the 1.97 Å (Ti-O bond length). The presence of an V_O in the bulk results in the loss of two Ti-O oxygen bonds and two overlapping peaks appear at 4.21 Å, which come from the distance between Ti and its second nearest neighbor O, as shown in Fig. 5 (a). Due to the influence of GBs, the PDFs of V_O are mostly different from the bulk. Interestingly, we find that an V_O in layer 0, retains the V_O PDF with two second nearest neighbor bond lengths in its six nearest neighbor PDF [see Fig. 5 (b)]. Here, the contribution of the GB is to slightly shorten the Ti-O second nearest neighbor distance. Nevertheless, despite the structural similarities between an V_O at the GB and the bulk, the presence of the GB seems to have an overall repulsive interaction with the V_O . Conversely, for V_O in layer 1, three V_O related peaks are observed [see Fig. 5 (c)]. Unlike bulk $SrTiO_3$, two of the vacancy related peaks are only slightly shifted away from the optimal Ti-O position, while only one second nearest neighbor peak emerges. This is a result of the large relaxation of the mirror symmetric O atoms (1s, its original position is also shown in Fig. 1). This relaxation now allows for Ti ions near the interface to achieve their

preferred six-fold coordination and is the reason for the large GB stabilization and segregation energies observed for V_O in layer 1. In layers 2 and 3, we observe a splitting of the second-nearest neighbor peak. This undoubtedly creates some local polarization within the lattice, which can then interact with the grain boundary. This lattice polarization is again indicative of the preference for local structure distortions, such that Ti ions can obtain their preferred six-fold coordination with near-neighbor oxygen ions. This is a consequence of the relationship between valence and bond-length as described in the bond-valence theory [34], which has been previously shown to dictate the local structure distortions in bulk perovskites [35-36]. The influence of the GB on the Ti-O bond lengths becomes weaker for V_O further away from the GB returning to the bulk arrangement by layer 10 (not shown here).

The above relaxation effects can be calculated quantitatively. When an V_O forms, the chemical bonds of the oxygen atom are broken, yielding the bond energy, E_b ; at the same time, the local geometry relaxes proving a relaxation energy, E_r . Based on this process, the relationship $E_{seg} = E_b + E_r$ is obtained, in which the values of E_b and E_r are referenced to their bulk values, similar to E_{seg} . Fig. 2 (b) shows the layer dependent values of E_b and E_r for V_O^{2+} . We observe that the relaxation energy of layer 1 is more negative than that of the others. The origin of this effect is the close proximity of the pair of oxygen ions on either side of the GB (1 and 1s, Fig. 1). As one of the oxygen atoms in the pair is removed, the other oxygen ion relaxes considerably, to a position in the mirror plane (i.e., along the GB), as shown in the inset of Fig. 5 (c) and the Ti is now able to achieve its preferred coordination with the surrounding O ions. A similar process is also observed for the V_O in layer 2. When an O atom (2 in Fig. 1) is removed, the mirror symmetric O (2s in Fig. 1) relaxes to a position close to but out of the GB (the inset of Fig. 4 (d)),

which has a relaxation energy less negative than V_O in layer 1, but more favorable than V_O in the others. Again, this is a direct consequence of the preference towards maintaining the six-fold coordination which is now mediated by the presence of a GB within these materials. It is worth noting that layer 4 also has a negative V_O segregation energy. This is a direct consequence of the interplay between the local bonding environment and the distance from the GB. Specifically, the local environment of V_O is similar to that of bulk; resulting in similar relaxation energies. On the other hand, the proximity to the GB results in an enhancement in the bond energy. Overall, this enhances V_O segregation to this layer.

3.2 Migration of oxygen vacancy

The diffusion mechanism for V_O towards and away from the $\text{SrTiO}_3 \Sigma 3 (112) [\bar{1}10]$ tilt GB is as important as its segregation. Since V_O^{2+} is the dominant point defect under most conditions, we only investigate the energetics of V_O^{2+} diffusion along the $\langle 110 \rangle$ diffusion path, which is the preferred migration path in this material [37]. For comparison, the diffusion of V_O^{2+} in bulk SrTiO_3 was also examined using a supercell having the same dimensions as that for GBs study. The migration barrier was determined to be 0.74 eV, in good agreement with the experimental value of 0.86 eV [38].

In the case of the GB, V_O^{2+} diffusion “perpendicular” to $\Sigma 3 (112) [\bar{1}10]$ tilt GB was studied. This is the diffusion across the different layers, i.e. from oxygen 0 to 10 or from oxygen 10 to 0 in Fig. 1. Fig 6 depicts the layer-dependent segregation energies (short solid lines) and migration barriers (stars) for V_O^{2+} . In figure 6, all segregation energies and migration barriers are relative to layer 10, similar to bulk. Meanwhile, the migration barriers, which are relative to the starting V_O^{2+} position of each migration path, are summarized in table I. For instance, a migration barrier from layer 0 to layer 1, label $D_{0,1}$, is reported relative to the segregation energy

of layer 0, while the reverse direction, $D_{1,0}$, is relative to layer 1. We find that the barriers for V_O^{2+} diffusion across layers 3 to 10, ranges from 0.39 to 1.08 eV, with no preferential diffusion direction.

Near the interface, however, we find a general tendency for V_O^{2+} to diffuse towards layer 1. Specifically, we observe that the barriers for V_O^{2+} diffusion from layer 0 ($D_{0,1}$) and layer 2 ($D_{2,1}$) to layer 1 and from layer 3 to layer 2 ($D_{3,2}$) are relatively low, only 0.09 eV and 0.31 eV, 0.46 eV, respectively. In contrast, diffusion away from layer 1 results in extremely high barriers; 2.75 eV and 1.42 eV for $D_{1,0}$ and $D_{1,2}$, respectively. These results indicate that oxygen vacancies in the layers adjacent to layer 1 (2, 3 and especially 0 layers) will migrate to layer 1 even if there is a small energy fluctuation and become trapped. Interestingly enough, the V_O^{2+} in layer 1 also has very low diffusivity parallel to the GB. For the $\langle 110 \rangle$ diffusion of V_O^{2+} in layer 1 (Fig. 7 (b)), which is parallel to the $\Sigma 3$ (112) $[\bar{1}10]$ GB, we compute an energy barrier of 1.33 eV. Although this barrier is lower than $D_{1,2}$ and $D_{1,0}$, it is still much higher than that in the bulk (0.74 eV).

The trapping mechanism of V_O^{2+} at layer 1 can again be readily understood through an analysis of the local structure changes. As shown in Fig. 7 (a) to (c), the diffusion of V_O^{2+} in layer 1 along any direction must involve the simultaneous displacement of a number of atomic species. During these multi-atomic-displacement processes, the symmetric structure of V_O^{2+} in layer 1 is broken resulting in a reduction in the Ti coordination with oxygen ions. As discussed earlier, this six-fold coordination of Ti is the origin of the strong segregation of V_O^{2+} in layer 1. As such, any deviation away from this bonding condition (e.g. the migration of an V_O^{2+} away from layer 1) will result in a significantly high energy cost.

4. Conclusions

The segregation of oxygen vacancies, V_O , in the vicinity of the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB in $SrTiO_3$, has been studied using density functional theory calculations. A strong tendency for the V_O to segregate to the first neighbor layer of the grain boundary and its important role on the grain boundary stability are predicted. Meanwhile, the diffusion mechanisms for the V_O^{2+} in the vicinity (among layers 0 to 3) of the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB are found to differ from the bulk. An V_O^{2+} in the layers adjacent to layer 1 easily migrates to this layer and is subsequently trapped. The segregation and trapping of oxygen vacancies in the first neighbor layer of grain boundary is attributed to the large relaxation of its GB mirror symmetric O towards the GB; thereby recovering the six-fold coordination of the Ti ions at the GB. The diffusions of V_O^{2+} out of or along layer 1 is a multi-atomic-displacement process, which breaks the symmetric structure of the V_O^{2+} in the layer, reducing the coordination of interfacial Ti with oxygen ions, thus resulting in very high barriers for diffusion.

The results of this work could be useful for engineering electronic, transport, and capacitive properties of $SrTiO_3$ by controlling GB structure and grain size or layer thickness. In nanocrystalline $SrTiO_3$, The density of $\Sigma 3$ (112) $[\bar{1}10]$ tilt GBs is expected to have significant effect on the diffusivity of V_O^{2+} . Higher V_O^{2+} diffusivity as a result of the low GB density will advance the application of $SrTiO_3$ as an oxygen ionic conductor; while lower V_O^{2+} diffusivity as a result of the high GB density may be beneficial for preventing the electrical degradation of the dielectric [10,39,40]. Furthermore, the significant influence of the GB on the electronic acceptor/donor levels of the oxygen vacancy may guide the control of the optical properties and conductivity in $SrTiO_3$. Lastly, such a phenomenon is also expected to occur in other oxides. Fully understanding the distribution and diffusion mechanisms of point defects both in and near

the interfaces of materials is crucial to the engineering of material properties. Thus, this study is expected to stimulate further systematical investigations on the point defect - grain boundary interaction in oxides.

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Table I Migration barriers (eV) of V_O^{2+} . $D_{m,n}$ means the diffusion from layer m to layer n, referring to Fig. 6.

Paths	E_m (eV)	Paths	E_m (eV)
$D_{0,1}$	0.09	$D_{1,0}$	2.75
$D_{1,2}$	1.42	$D_{2,1}$	0.31
$D_{2,3}$	0.67	$D_{3,2}$	0.46
$D_{3,4}$	0.90	$D_{4,3}$	0.98
$D_{4,5}$	1.08	$D_{5,4}$	0.39
$D_{5,6}$	0.92	$D_{6,5}$	0.86
$D_{6,7}$	0.79	$D_{7,6}$	0.94
$D_{7,8}$	0.75	$D_{8,7}$	0.67
$D_{8,9}$	0.71	$D_{9,8}$	0.77
$D_{9,10}$	0.64	$D_{10,9}$	0.87

Figure captions:

Figure 1 Configuration of the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB (O: red, Ti: gray and Sr: green). The numbers indicate the layer number for an V_O .

Figure 2 (a) The segregation energies of oxygen vacancies and (b) bonding and relaxation energies of V_O^{2+} in the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB as a function of the layer of the vacancy as defined in Fig 1.

Figure 3 Thermodynamic transition levels of V_O as a function of the layer of the vacancy.

Figure 4 The chemical potential and electron Fermi level dependent formation energies (E_f^{NGB} , J/m²) of the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB for an V_O at (a) the GB layer (layer 0) and (b) its 1st nearest-neighbor layer (layer 1).

Figure 5 Partial distribution function of Ti-O for various structures containing a point defect for V_O^{2+} . The corresponding relaxed local configurations of V_O^{2+} in each case are shown as an inset, in which the oxygen vacancy is represented by a yellow ball.

Figure 6 Layer dependent segregation energies (short solid lines) and migration barriers (stars) for V_O^{2+} . All segregation energies are referenced to V_O^{2+} at layer 10. $D_{m,n}$ means the diffusion from layer m to layer n . The dash line is a guide for the eyes.

Figure 7 Atomic displacements and barriers for an V_O^{2+} in layer 1 of the $\Sigma 3$ (112) $[\bar{1}10]$ tilt GB diffusing (a) to layer 0, $D_{1,0}$, (b) in layer 1, $D_{1,1}$ and (c) to layer 2 $D_{1,2}$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7