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LETTER TO THE EDITOR

First principles calculations of niobium substitution in strontium titanate

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Abstract

We have studied the effects of Nb incorporation in strontium titanate using DFT plane-wave pseudopotential calculations. Substitution of the impurity on a Ti site in the bulk crystal causes outward relaxations of the neighbouring Ti ions but does not affect the oxygen ions. A conduction band state localized on the Ti ions becomes occupied confirming the donor behaviour of the defect. The formation energy of the impurity is studied under different oxidation conditions. We have also studied the incorporation of Nb near to a $\Sigma = 3(111)$ grain boundary. The results indicate that Nb segregation is unfavourable due to Coulomb repulsion effects.

Strontium titanate (SrTiO_3) is an electroceramic perovskite material which exhibits a range of dielectric, ferroelectric and semiconducting properties. Its dielectric properties are commonly utilized in the form of grain boundary barrier layer capacitors [1]. The operation of these devices requires a polycrystalline component in which the grains are conducting and the grain boundaries are insulating. The effective dielectric constant of the material is determined by the average grain size, which should be large, and the average grain boundary width, which should be small. These microstructural characteristics are obtained using fabrication routes which usually involve the sintering of SrTiO_3 powder with several oxide additives [2, 3]. The high resistivity of the grain boundaries is obtained using oxides such as PbO , Bi_2O_3 , B_2O_3 and LiO which accumulate at the interfaces. The grains are typically made conducting by adding Nb_2O_5 which acts as a donor dopant and does not segregate to the grain boundaries. Oxides of other elements such as Ta, Y and La are also found to produce conducting grains. Native point defects in the material such as oxygen vacancies can further influence its electrical properties. Although the design of electroceramic materials for barrier layer capacitors is well established, it is largely dependant on a base of mainly empirical data. In order to further understand and optimize the material's electrical characteristics it is important to determine the electronic structure of the grains and their boundaries with and without dopant additives. In this paper we address this issue using first principles electronic structure calculations and focus, in particular, on the effects of incorporating Nb into bulk SrTiO_3 and also into a simple grain boundary.

Several experimental studies have shown that the incorporation of Nb into SrTiO₃ results in n-type material and that there is little or no observed segregation of the dopant to the grain boundaries [4]. The Nb⁵⁺ ion is assumed to substitute for the Ti⁴⁺ ion in the lattice. There are, however, no first principles calculations which provide for deeper understanding of this behaviour. Rodrigues *et al* [5] have used the DV-X α method to study Nb incorporation into the bulk and into the core of a [001] symmetric tilt boundary. However, they did not allow for atomic relaxation around the impurity and the model that they used for the tilt boundary structure was derived from an empirical pair potential calculation. Perhaps because of these approximations they found that Nb is only a weak donor in the bulk and that this weakness increases in the tilt boundary. In addition they did not report any information concerning the Nb formation energy in the bulk or the segregation energy in the tilt boundary. Thus the propensity for Nb grain boundary segregation was not established. In this letter, we employ density functional theory (DFT) to perform full relaxations around a Nb impurity in the bulk crystal and also in the core of a $\Sigma = 3(111)$ [10 $\bar{1}$] tilt grain boundary. This method gives accurate total energies as well information concerning the electronic structures of the defects. The $\Sigma = 3$ boundary geometry was chosen because of its relatively simple atomic structure which has been well characterized using both computational methods and high-resolution electron microscopy [6, 7].

The calculations are based on DFT [8] in the generalized gradient spin (GGS) density approximation using the Perdew–Wang functional and were performed using the Accelrys CASTEP software¹. Vanderbilt ultrasoft pseudopotentials [9] available with the software were used. The explicitly treated valence states for Sr were 4s, 4p and 5s, for O 2s and 2p, and for Ti 3s, 3p, 3d and 4s. The Kohn–Sham wavefunctions were expanded in plane waves and the electronic ground state was reached using a conjugate gradients algorithm. Monkhorst–Pack meshes were used for the Brillouin zone sampling [10]. The electron partial densities of states, Mulliken charges and bond overlap populations were calculated using a technique based on projecting the plane-wave Kohn–Sham eigenstates on to atomic orbital basis sets [11, 12].

At room temperature SrTiO₃ has a cubic perovskite structure. The experimental lattice parameter is $a_{0,exp} = 3.905$ Å [13] and our DFT–GGS result of 3.93 Å is in excellent agreement with this. We used a 120-atom supercell for most of our calculations and the Nb substitution was performed by replacing one Ti atom near its centre. The supercell had an hexagonal shape to accommodate the geometry of the $\Sigma = 3$ grain boundary. We studied only Nb_{Ti} since Nb has a formal valency of +5 making it very unlikely to substitute on any other site. In this model, the distance between the Nb_{Ti} and its periodic images was $2\sqrt{2}a_0 = 11.14$ Å. In our earlier study on oxygen vacancies in SrTiO₃ [14, 15] we found that a defect separation of $2a_0$ was sufficient to minimize intercellular interactions. Since the lattice perturbations around the Nb impurity are found to be much smaller than around the vacancy, we conclude that the impurity is well isolated in this letter. The resulting Nb/Ti ratio in the 120-atom supercell is 1/23.

The grain boundary was created in the supercell by performing a twinning operation about the (111) plane. Because of the periodic border conditions, this resulted in two symmetry equivalent boundary structures. The boundary core of each structure consisted of a SrO₃ plane and the Nb impurity was placed on one of the Ti sites in the (111) plane neighbouring the Sr–O terminated core. The relaxed atomic structure of the cell containing a Nb-doped grain boundary is presented in figure 1. The separation between the two grain boundaries in the supercell is 6.9 Å and the distance between the Nb impurity and its periodic images in the boundary plane is 11.23 Å. The Nb/Ti ratio in the doped (111) layer is 1/3. A smaller

¹ CASTEP 3.9 and 4.2; CERIU² (Accelrys).

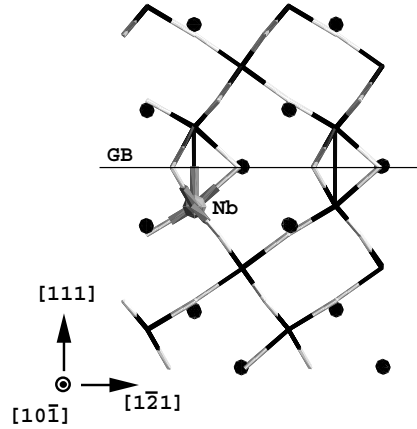


Figure 1. The atomic structure of the $\Sigma = 3(111)$ grain boundary in SrTiO_3 showing the relaxed 120-atom supercell geometry. The doped grain boundary plane is indicated by GB and the site chosen for Nb substitution is shown. The Sr ions are represented by dark spheres and the Ti–O sublattice is represented by dark and light cylinders.

60-atom model was also studied in which the grain boundary separation was 13.6 Å. In this case the incorporation of an impurity results in an entire Nb monolayer next to the grain boundary.

The electron kinetic energy cutoff was set to 400 eV. For the 60-atom models the point group symmetry was fixed after initial coarser relaxation and we used a symmetrized $4 \times 4 \times 1$ k -point mesh for the Nb-doped grain boundary and a $4 \times 4 \times 2$ k -point mesh for the bulk SrTiO_3 and stoichiometric grain boundary models. The gamma point approximation was used for the 120-atom model and a Fermi level smearing of 0.05 eV was employed to improve the convergence. In all models the supercell angles were fixed.

The formation energy (E^F) of the Nb impurity in the bulk crystal was calculated as follows:

$$E^F = E_{\text{Nb}}^0 - E^0 + \mu_{\text{Ti}} - \mu_{\text{Nb}} \quad (1)$$

where E_{Nb}^0 and E^0 are the total energies of the Nb-doped and undoped bulk supercells respectively, and μ_{Ti} and μ_{Nb} are the chemical potentials of Ti and Nb. The chemical potentials are estimated using various Ti sinks and Nb sources as described later. The segregation energy (E^S) of the Nb impurity to the grain boundary was calculated using

$$E^S = (E_{\text{Nb}}^{GB} - E_{\text{Nb}}^0) - (E^{GB} - E^0) \quad (2)$$

where E_{Nb}^{GB} and E^{GB} are the total energies of the Nb-doped and undoped grain boundary supercells respectively.

The partial densities of states for pure and Nb-doped bulk SrTiO_3 are presented in figures 2 and 3. In pure SrTiO_3 , the valence band consists of O p states which are hybridized with Ti d states. Doping the crystal with Nb introduces Nb d states which are split between the valence and conduction bands. A similar result was found by Rodrigues *et al* [5] although in their case the Nb d valence states were located 8 eV below the Fermi energy while in this letter the impurity band is centred around 6 eV and is significantly broader. The Nb d and O p states are also hybridized as indicated by the computed overlap population of the Nb–O bond which is 0.66. The conduction band of the Nb-doped crystal consists of Ti d states, a small component of O p states due to the hybridisation and Nb d states. The Ti d conduction band spectrum for an atom neighbouring the impurity is considerably narrower than for a Ti atom in the pure bulk environment as seen from comparing figures 2 and 3.

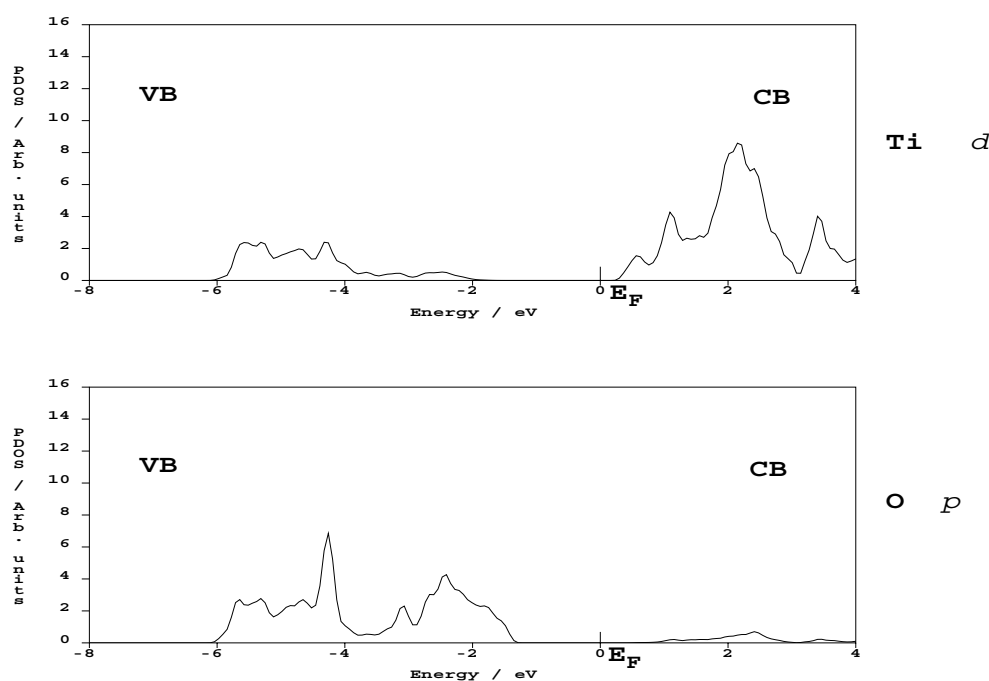


Figure 2. The partial density of states near the Fermi level for bulk SrTiO₃ obtained using the 120-atom supercell. For simplicity, only the Ti d states and O p states are shown.

The Kohn–Sham eigenvalues indicate that the Nb substitution causes the six lowermost conduction bands to become partially occupied. These states are almost degenerate with occupancies of 0.34 and 2×0.18 for the three spin up Kohn–Sham eigenstates, and 0.13 and 2×0.08 for the three spin down eigenstates. Thus, the superposition of these eigenstates forms an occupied spin polarized conduction band state. This state distributes over the Ti sites but is absent from the Nb site as can be seen from the spin up and down electron density difference plot in figure 4. Furthermore, the spin down component of the wavefunction leads to a small negative polarization at the O sites.

In general, the atomic relaxations due to the Nb substitution are small. The Nb–O bond lengths (1.97–1.98 Å) are close to the bulk Ti–O value (1.96 Å). This indicates that the O²⁻ ions feel a Coulombic attraction towards the large positive charge on the Nb ion which is balanced by its large ionic radius. This is evident in the overlap populations of the Nb–O bonds (0.66) which are somewhat larger than that of the bulk Ti–O bond (0.52). The O ions cannot completely screen the large positive ionic charge of Nb and the nearest Ti atoms are repelled slightly. The Ti–O bond length for the neighbouring O atoms increases to 2.02 Å and the overlap population decreases to 0.49. The Sr–Nb interatomic distance is 3.44 Å, which is also larger than the bulk Sr–Ti distance of 3.40 Å.

The results presented above would imply that Nb should not segregate to compact and coherent grain boundaries due to the Coulomb repulsion between cations and the impurity. To demonstrate this we have considered Nb substitution on a Ti site adjacent to the core of a $\Sigma = 3(111)$ twin boundary (figure 1). This interface has a highly ordered and bulk-like structure. However, the twinning brings two Ti atoms on opposite sides of the boundary closer to each other than they would be in the bulk (2.68 Å after relaxation). Consequently the

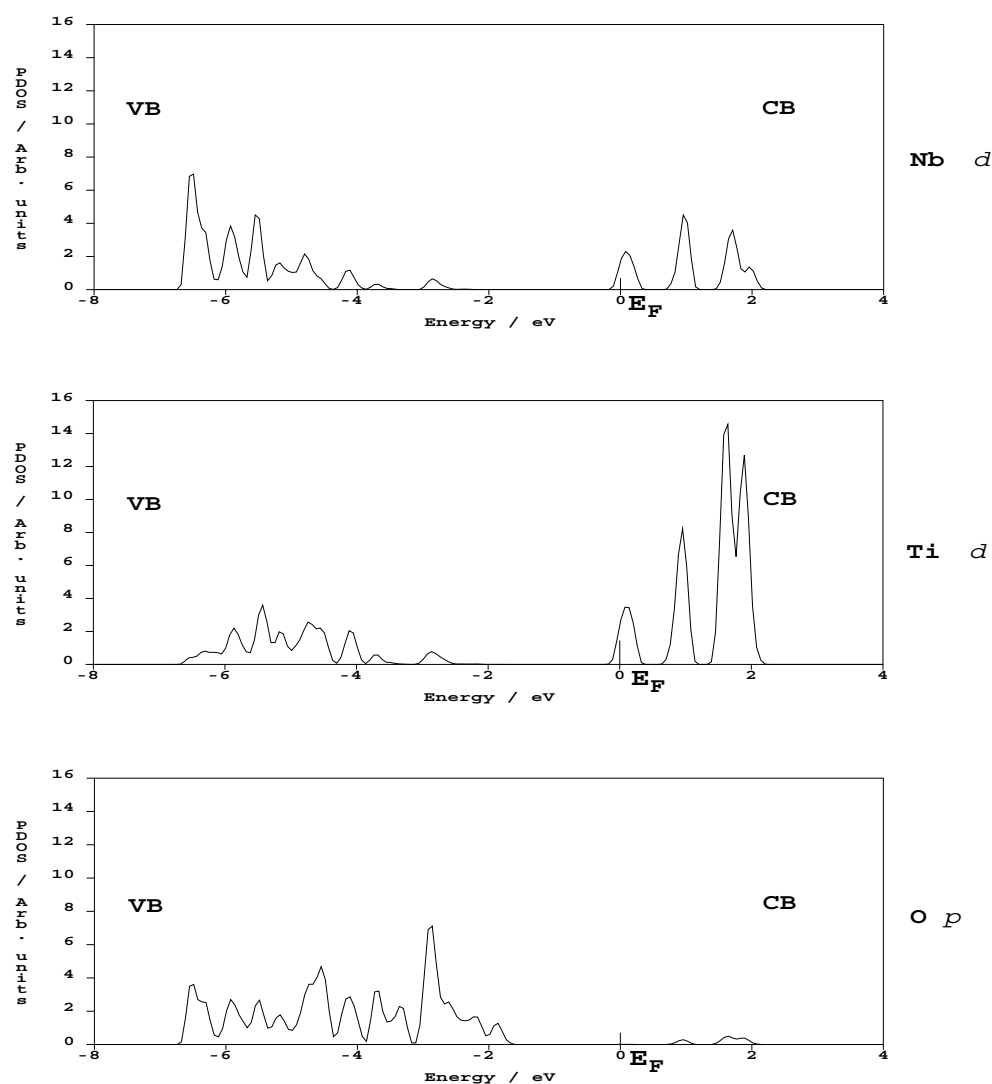


Figure 3. The partial density of states near the Fermi level for Nb-doped bulk SrTiO₃. The d states on the Nb atom are shown together with the p states on a O atom neighbouring the impurity and the d states on a Ti atom neighbouring the impurity.

substitution of a more positively charged atom on one of these Ti sites would increase the Coulomb repulsion. This is supported by the calculated segregation energy for these sites which is +0.24 eV. The positive sign means that additional energy is required for segregation. The Ti–Nb bond length across the grain boundary is 2.76 Å and the electrons there are in a highly anti-bonding state since the overlap population is -0.98 . The corresponding Ti–Ti bond length across the undoped grain boundary is 2.68 Å and the Mulliken analysis shows that these atoms are also anti-bonding with an overlap population of -0.94 . However, the donor character of the Nb ion is enhanced since its Mulliken charge increases from $0.85e$ in the bulk to $0.95e$ in the boundary.

To further examine the nature of Nb segregation to the grain boundary we repeated the calculations using a 60-atom supercell. In this smaller model the effective impurity

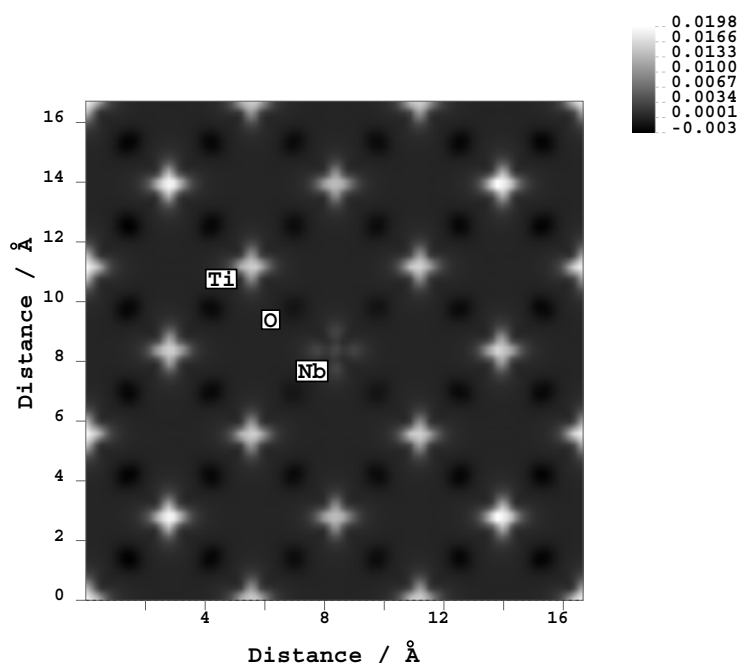
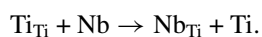
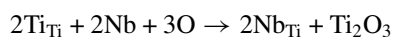
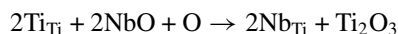
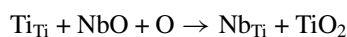
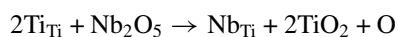


Figure 4. The spin up and down electron density difference in the Nb-doped bulk crystal. A slice through the (100) TiO₂ plane coinciding the Nb impurity is presented. The occupied conduction band states are found to be spin polarized and therefore the variation in the spin density displays the spatial distribution of these states. The scale is in $e\text{\AA}^{-3}$.

concentration at the boundary increases since an entire monolayer of Nb is formed adjacent to the boundary plane. With a complete layer of Nb next the boundary, the structure should relax more easily by rigid translations of atom planes normal to the interface and this is indeed observed during the energy minimization. Whilst the Ti–Nb distance across the boundary is found to increase by 0.08 \AA as it did in the larger model, the Sr cation in the grain boundary plane also relaxes and moves 0.07 \AA away from the Nb plane in a direction normal to the boundary. This additional relaxation was not observed in the 120-atom supercell and has the effect of lowering the segregation energy by 0.21 eV . Thus, the smaller supercell calculation shows that although the additional Nb–Nb interactions and the response of the Sr ions reduce the segregation energy, it is still positive and monolayer formation is unfavourable.

The formation energy of Nb in bulk SrTiO₃ was estimated using various Nb sources and Ti sinks with different metal/oxygen ratios. Metallic Nb and Ti, NbO, ζ -Nb₂O₅, TiO, TiO₂ (rutile) and Ti₂O₃ were chosen. The relative stabilities of these different Nb and Ti compounds depend on the oxygen chemical potential μ_{O} , which was treated as a variable. Depending on the value of μ_{O} , i.e. whether the conditions are oxidizing or reducing, different Ti sinks and Nb sources were energetically preferred and following reactions were found to be favourable:



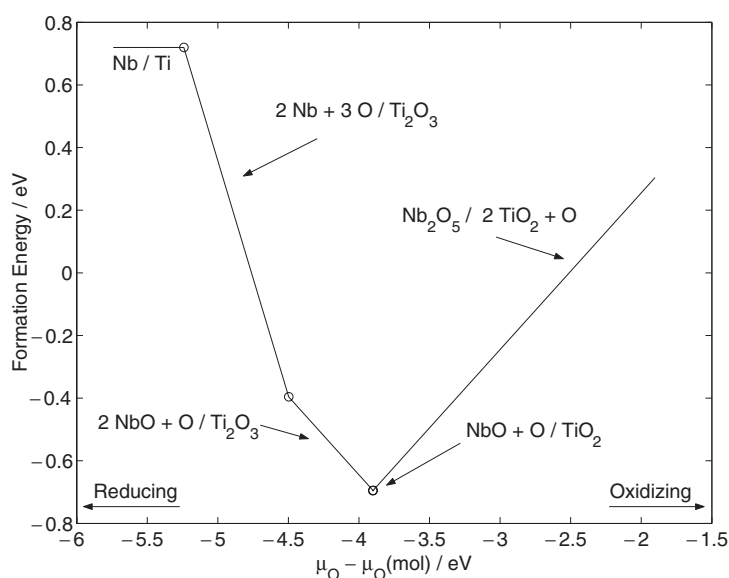


Figure 5. The formation energy of the Nb_{Ti} impurity as a function of oxygen chemical potential for calculated lowest energy Nb sources and Ti sinks. The x -axis is scaled so that the calculated chemical potential μ_{O} (mol) of an O atom in an isolated O_2 molecule is zero. The reaction $\text{Ti}_{\text{Ti}} + \text{NbO} + \text{O} \rightarrow \text{Nb}_{\text{Ti}} + \text{TiO}_2$ is preferred only in a very narrow region around $\mu_{\text{O}} = -3.9$ eV.

In figure 5 we have plotted the Nb_{Ti} formation energy for the lowest energy pairs of Ti sinks and Nb sources as a function of μ_{O} for each of these reactions. The energy of an isolated O_2 molecule was also calculated as a reference.

In summary, we have used a DFT-based first principles computational method to model the incorporation of Nb into SrTiO_3 . Substitution on a Ti site has been assumed and full atomic relaxations have been performed both in the bulk crystal and at a grain boundary. In the bulk crystal, the atomic structure is only weakly perturbed by the substitution and consists mainly of nearest neighbour Ti ions moving away from the Nb atom. The relaxations of the neighbouring O ions are negligible. The mutual repulsion between the Nb and the Ti ions would indicate that Nb is unlikely to segregate to compact grain boundary structures, at least in close proximity to cation species. We have demonstrated this using the highly ordered and coherent $\Sigma = 3(111)$ twin boundary where the segregation energy is found to be positive and the Nb and Ti ions facing each other across the boundary move apart.

The electronic structure of the doped bulk crystal shows an almost completely occupied conduction band state which is localized only on Ti sites and not on the Nb site. Therefore the Nb site behaves as a single donor. This contradicts the result of Rodrigues *et al* [5] who observed a net loss of only $0.4e$ from the Nb atom and claim that Nb is only a weak donor. However, they did not relax their atomic structure which may explain the discrepancy. The relaxations of the Ti ions screen and reduce the positive ionic Coulomb potential due to the Nb substitution and therefore the electrons are less attracted to this region. The partial densities of states qualitatively agree with the results of Rodrigues *et al* [5] and the Nb d states are split between the valence and conduction bands. However, the exact position of the Nb d valence band states is found to be almost 2 eV closer to the Fermi level than determined by Rodrigues *et al* [5] and are broadened. The valence band consists mostly of O p states which are hybridized with both the Ti and Nb d states in the conduction band. In addition,

we have estimated the formation energy of Nb_{Ti} to increase in oxygen reducing conditions. Our results confirm the donor nature of the Nb ion and provide new information about its electron-level properties and segregation behaviour. We have confirmed that Nb is unlikely to segregate to grain boundaries with compact structures but further studies are needed to examine the segregation behaviour of more open or oxygen-rich grain boundary structures.

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