DFT study of Se and Te doped SrTiO$_3$ for enhanced visible-light driven photocatalytic hydrogen production

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Abstract

The pure STiO$_3$ has been experimentally demonstrated to catalyze H$_2$ production using water splitting, but the reaction can only be driven by Ultraviolet (UV) radiation due to the large band gap of SrTiO$_3$. This motivated us to search efficient strategy to tune its band gap, so that it can function in the visible region of the solar spectrum. In this study, the electronic, optical and photocatalytic properties of Se-doped, and Te-doped SrTiO$_3$ has been investigated using density functional theory (DFT) within the generalized gradient approximation (GGA). Our results reveal that the effect of doping can lead to band gap narrowing without introducing any isolated mid-gap states. This improves greatly the visible light activity of SrTiO$_3$ and depresses the recombination of photogenerated electron–hole pairs. Furthermore, the locations of calculated band edges relative to the water reduction and oxidation levels for doped systems meet the water-splitting requirements. Consequently, our results show that the performance of SrTiO$_3$ for hydrogen generation by photocatalytic water splitting is significantly enhanced with Se and Te doping. In particular, Te doping can enhance greatly the visible light photocatalytic activity of SrTiO$_3$. We expect this study can provide a theoretical basis for a prospective experimental works.

Keywords SrTiO$_3$ · Doping · DFT · Visible light · Photo-catalytic hydrogen production · Water splitting

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1 Introduction

With the continuous increasing demand for the energy as a consequence of rapid demographic, economic and social developments, the energy supply should be permanently and sufficiently provided. However, nowadays, the main energy supply comes from fossils, that are not renewable and have disastrous impacts on the environment and climate change. Consequently, Hydrogen energy is considered as a clean and sustainable energy carrier of the future. The most economic method to produce hydrogen is the photocatalytic splitting of water using sunlight. Hence, this has inspired large research efforts into designing and improving a wide range of photocatalytic systems over the past few decades. Most of these systems are metal oxide semiconductors. For example, titanium dioxide (TiO$_2$) has been widely used for water splitting (Zhu et al. 2016) and contaminants treatment in air and water (Dulian et al. 2019). Besides, ABO$_3$-type perovskite oxides have gained a huge interest due to their low cost, high stability and non-toxicity. The main shortcoming which restricts their application at a large scale is their large band gap (superior to 3 eV) which makes them active only in the UV region of the solar spectrum. Fortunately, this limitation can be overcome by employing adequate dopant elements. This can regulate the band-gap to an appropriate level that enables the absorption of visible light. In the present work, we are concerned with narrowing the band gap of SrTiO$_3$ (3.15 eV), which has been investigated widely in the field of production of hydrogen from water splitting.

In fact, several studies showed that adjusting SrTiO$_3$ through doping has proved to be inexpensive, effective, easy to handle and constitutes a successful way to redshift its absorption spectrum, which may increase its visible light activity and enhances its photocatalytic efficiency. For example the n-type Nb-doping of SrTiO$_3$ in the Ti site, shows strong absorption in the visible light region and higher photo-catalytic activity (Shujuan et al. 2016). Zhou et al. (2018) synthesized Er$^{3+}$-doped SrTiO$_3$ nanoparticles, they found that the doped SrTiO$_3$ exhibits higher photocatalytic activity for hydrogen production under simulated solar irradiation compared to undoped SrTiO$_3$. In order to develop the SrTiO$_3$ photocatalyst for photodegradation of Rhodamine B solution, Wang et al. (2020) investigated the photocatalytic properties of SrTiO$_3$ powders doped with Eu$^{3+}$ ion. The study revealed a band gap narrowing owing to the hybridization of Eu d-states with the Ti 3d or O 2p orbitals, which results in a remarkable improvement of light absorption capability in the visible light region of doped system compared to the pure one. Thanh et al. (2014) studied the influence of Mn doping on the structural, optical and magnetic properties of SrTi$_{1-x}$Mn$_x$O$_3$ (x = 0.0–0.1) synthesized by a solid-state reaction method. They found that an increasing of Mn concentration in the host material, leads to a significant band gap narrowing, which shifts the absorption spectrum of SrTiO$_3$ to the visible wavelengths range, and increases its photocatalytic performance.

In general, doping strategy enhances the photocatalytic properties of semiconductors through narrowing the band gap by lowering the CB, raising the VB, and/or inducing mid-gap states. However, it is well known that inducing mid-gap states associated with some types of monodoping, minimizes the photoconversion efficiency by trapping the photogenerated charge carriers. For example, in an experimental and theoretical study, Bae et al. (2008) showed that doping noble metals (Ru, Rh, Ir, Pt, Pd) in the perfect SrTiO$_3$ introduces new energy levels between the VBM and CBM. This improves the photon harvesting ability, but does not guarantee an improvement in photocatalytic H$_2$ generation, because these mid-gap levels act as trapping centres, which promote the unfavourable effect of recombination. Also, Chen et al. (2012) studied the effect of doping by Ru on the photocatalytic
activity of SrTiO₃ based photocatalyst using DFT calculations. They found that the mid-gap states introduced by Ru dopant promote faster charge carriers recombination.

To avoid the formation of mid-gap states introduced by some dopants, researchers tend to choose codoping with two different types of elements. For example, it has been reported that codoping of Ta or Sb and Cr into the pure SrTiO₃, exhibited a higher efficiency in H₂ evolution. By codoping Ta⁵⁺ or Sb⁵⁺ to Sr sites and Cr³⁺ in the Ti sites, it is able to establish the charge compensation (Ishii et al. 2004; Kato and Kudo 2002). Besides, Miyauuchi et al. (2004) and Wang et al. (2005) successfully prepared (La, N) codoped SrTiO₃, they found a decrease in the possibility of structure defects and an improvement in the photocatalytic activity under visible light towards H₂ evolution process. This is because the codoping of La³⁺ ions in Sr²⁺ sites and N³⁻ in O²⁻ sites maintained the charge compensation and minimized the generation of O vacancies. Furthermore, it has been demonstrated in a theoretical investigation by Wei et al. (2010) that codoping of either nonmetal (H, F, Cl, Br, I) or metal (V, Nb, Ta, Sc, Y, La) is a successful way to passivate the N-induced ingap states. Their study aims at exploring the codoping synergistic effects for higher energy conversion efficiency.

Generally, the formation of mid-gap states is associated with the charge imbalance introduced by the aliovalent dopants. According to our previous work (Bentour et al. 2020), the bandgap of SrTiO₃ was narrowed in the case of the substitution of S²⁻ for O²⁻. Besides the band gap of S-doped SrTiO₃ is free from energy levels thanks to the same valence state of S and O. This can depress the undesirable electron–hole recombination in the crystal. Since, Se and Te are in the same group element with S and O in the periodic table of elements, and respectively possess the anionic (Se²⁻) and (Te²⁻) characters; therefore, doping by these anions on the O anion site is expected to give best results. Consequently, the present study is concerned with the investigation of the effect of anionic doping with Se and Te for the enhancement of visible light absorption as well as the photocatalytic performance of SrTiO₃ material. To our best knowledge, no experimental or theoretical work has been reported for these kinds of doping. We used DFT calculations to evaluate the stability, electronic, optical and photocatalytic properties of SrTiO₃, Se-doped SrTiO₃ and Te-doped SrTiO₃. We discussed the stability of the both doping cases based on the computed formation energies, and explored the band structures, density of states and electronic density distributions of pure and doped systems. Besides, we analysed the optical and photocatalytic performance for all systems based on their absorption spectra, variations of imaginary part of dielectric function and band alignment. Our findings show that the narrowing of band gap, absorption spectrum shifting into the visible light region and the photocatalytic performance of SrTiO₃ is further improved with Te doping compared to our previous study about (S, Mn)-codoped SrTiO₃ (Bentour et al. 2020). Our study serves to provide a theoretical basis for a possible experimental study.

2 Computational methods

We calculated the stability, the electronic and optical properties of pure, Se-doped and Te-doped SrTiO₃, using the full potential linearized augmented plane wave (FP-LAPW) method implemented in the Wien2K code (Blaha et al. 2001), within the framework of density functional theory (DFT), by treating the exchange and correlation in the level of the GGA-Perdew–Burke–Ernzerhof (GGA-PBE) approximation (Perdew et al. 1992). The basic quantities, electron densities and the potential are calculated in self-consistent manner. These quantities
are developed by dividing the unit cell into non-overlapping atomic spheres where a linear combination of radial functions times spherical harmonics is used with a cut-off parameter $l_{\text{max}} = 10$, and an interstitial region where a plane wave expansion is used with a cut-off parameter $R_{\text{MT}}^*K_{\text{max}} = 7$ (RMT is the smallest muffin-tin radius in the unit cell and $K_{\text{max}}$ is the magnitude of the largest K wave vector). The muffin-tin sphere radii used in the calculations are 1.63, 2.00, 1.70, 1.85 and 1.63 a.u. for respectively, Se, Te, Sr, Ti and O.

The results are obtained with an energy convergence criterion of $10^{-4}$ Ry. We used a $[7 \times 7 \times 7]$ grid with 51 special points for sampling the brillouin zone, corresponding to 800-k-points in the irreducible Brillouin zone.

In the calculations, $2 \times 2 \times 2$ supercells of cubic SrTiO$_3$ are constructed; one O atom is replaced by a Se or Te atom in the optimized geometry of supercells. The optimized pure, Se-doped and Te-doped SrTiO$_3$ supercells are shown in Fig. 1.

The absorption property of our systems can be explored using the complex dielectric function:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

The dielectric function was calculated in the momentum representation, which requires matrix elements of the momentum between occupied and unoccupied eigen states. The real part of the dielectric function $\varepsilon_1(\omega)$ is obtained from Kramers–kronig transformation (Zaari et al. 2014):

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega'$$

and the imaginary part $\varepsilon_2(\omega)$ is obtained by summation over the empty states (Okoye 2003):

$$\varepsilon_2(\omega) = \left( \frac{4\pi e^2}{\omega^2 m^2} \right) \sum_{i,j} \int i |M| f_i(1 - f_j) \ast \delta(E_j - E_i - \omega) d^3k$$

where $p$ is standing for the principal value of the integral, $e$ is the elementary charge, $m$ is the electron’s mass, $M$ is the dipole matrix element, $i$ and $j$ are respectively, the initial and final states, $f_i$ is the Fermi–Dirac Distribution Function for the $i$-th state and $E_i$ is the energy of an electron in the $i$-th state with a wave number $k$.

Indeed, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, parts allow one to find many optical properties, like absorption coefficient $\alpha(\omega)$ using the following formula (Bhattacharya 2015):

Fig. 1 The optimized $2 \times 2 \times 2$ supercell of: a pure, b Se-doped and c Te-doped SrTiO$_3$, respectively
3 Results and discussion

3.1 Defect formation energy

The defect formation energy calculation provides insight information about the experimental growth possibility of a material. In fact, the lower the formation energy is, the easy feasible and more stable the doping structure is (Zhou et al. 2011).

To calculate the defect formation energy for the doped materials, the following formula is used:

$$E_f = E_{doped} - E_{undoped} + \mu_O - \mu_M$$  \hspace{1cm} (1)

where $E_{doped}$ and $E_{undoped}$ are the total energies of the supercell with dopant and without it, respectively. $\mu_M$ (M = Se, Te) and $\mu_O$ are the chemical potentials of the dopants (Se and Te) and O, respectively. The value of $\mu_{Se}$ and $\mu_{Te}$ is calculated from bulk trigonal selenium (Cherin and Unger 1967) and rhombohedral form of tellurium (Bradley 1924), respectively, while $\mu_O$ is calculated from the energy of a O$_2$ molecule centred in a cubical box of $15 \times 15 \times 15$ Å$^3$ as $\mu_O = \frac{1}{2} \mu_{O_2(gas)}$. As we know the formation energy depends on the growth conditions. Therefore, we have examined the Ti–rich and the O–rich conditions. In fact, in a state of thermodynamic equilibrium, the following condition must be satisfied between SrTiO$_3$ and the reservoir of Sr, Ti and O.

In the case of equilibrium between SrTiO$_3$ and reservoir of Sr, Ti, and O, one has the following formula:

$$\mu_{Sr} + \mu_{Ti} + 3\mu_O = \mu_{SrTiO_3(bulk)}$$ \hspace{1cm} (2)

In a Ti–rich environment, the $\mu_{Ti}$ chemical potential is supposed to be the energy of bulk Ti, while the $\mu_O$ chemical potential is deduced from Eq. (2). In an O–rich environment, the $\mu_O$ chemical potential is calculated as previously mentioned, while $\mu_{Ti}$ is achieved from Eq. (2). The $\mu_{Sr}$ is calculated from the energy of the Sr atom in the bulk crystal. The results are shown in Table 1.

Table 1 shows that the formation energies are positive for all types of doping and in both conditions, with some preference for the Ti–rich condition, which means that making these compounds in experiment requires energy from the surroundings. Besides, Se-doped SrTiO$_3$ is easy feasible compared to the Te-doped SrTiO$_3$, which can be explained by that the ionic radius of Se$^{2-}$ is smaller than that of Te$^{2-}$.
3.2 Electronic properties

In order to examine the effect of selenium doping and tellurium doping on the SrTiO$_3$ electronic properties, we calculate the band structures and partial density of states (PDOS) for pure, Se-doped and Te-doped SrTiO$_3$. The calculated band structures are shown in Fig. 2.

We see that the overall band aspect for the pure SrTiO$_3$ (Fig. 2a) is in good agreement with previous calculated band structures (Zhang et al. 2013). Besides, its band gap is direct at the $\Gamma$ point, and with value of about 1.80 eV, which is in line with previous computational results (Wei et al. 2009). The observed underestimation in the band gap value compared to the experimental value (3.15 eV) (Thanh et al. 2014) is due to the well-known
limitation of GGA (Godby et al. 1986). After doping with Selenium (Fig. 2b), and with tellurium (Fig. 2c) we remark that the band gap is still direct but it is narrowed by about 0.52 eV, and 1.04 eV, respectively. As a result, the energy required to pass an electron from the valence band to the conduction band was significantly decreased from the undoped system, to the doped with Se to the doped with Te; this can red-shift the optical absorption edge of SrTiO$_3$ and improves its visible light activity progressively in this order. Besides, no in-gap states appeared; Which can be explained by that the number of valence electrons in the crystal remains the same after substituting an O atom with a Se or Te one, due to the similarity of valence shells of Se (4s$^2$4p$^4$), Te (5s$^2$5p$^4$) and O (2s$^2$2p$^4$); this helps to reduce the effect of recombination between the electrons and holes. Therefore, the photo-catalytic efficiency of these doped systems is improved.

The calculated (PDOS) for pure, Se-doped and Te-doped SrTiO$_3$ are presented in Fig. 3. It is shown that the valence band maximum (VBM) of pure SrTiO$_3$ is dominated by O 2p states, while its conduction band minimum (CBM) is consisted of Ti 3d states. Besides, the VBM of Se-doped SrTiO$_3$ is consisted from O 2p and Se 4p states, while its CBM is contributed primarily by Ti 3d states. For Te-doped SrTiO$_3$ the VBM is consisted from O 2p, Te 5p and some Ti 3d states, whereas its CBM is mainly consists of Ti 3d states.

In order to reveal the origin of band gap narrowing observed in doped compound, let’s go back to the previous band structures, we see that there is a split in the levels of VBM and CBM for all compounds, which can be explained by the crystalline field that reigns...
inside, and the existing mutual electrostatic interactions in the CBM in-between Ti 3d states for all materials and in the VBM in-between O 2p states for the pure material, in-between O 2p and Se 3p states for the Se-doped material and in-between O 2p, Ti 3d and Te 6p states for the Te-doped material. However, the CBM and VBM for both Se-doped and Te-doped SrTiO$_3$ are more dispersive compared to these of pure SrTiO$_3$, which indicates that the covalency strength of the Ti–Se and Ti–Te bonds in doped systems is more than that of Ti–O bond in the pure SrTiO$_3$. This agrees with the obtained distribution of electronic density shown in the Fig. 4, where we see that the Ti–O bond is covalent in the pure SrTiO$_3$ (Fig. 4a) and the covalency strength increases with doping by Se and Te (Fig. 4b, c). Besides, we see that the Sr–O bond is ionic in pure SrTiO$_3$ (Fig. 4a') and its ionicity decreases with doping by Se and Te (Fig. 4b', c'). These variations in the covalency and ionicity strength of bonds can be explained by the lower electronegativity of Se and Te compared to that of O, and may be the origin of the observed band gap narrowing in selenium and tellurium doped SrTiO$_3$.

### 3.3 Optical properties

In order to investigate the effect of doping on the optical properties of SrTiO$_3$, the calculated imaginary part $\varepsilon_2(\omega)$ of dielectric function and absorption coefficient of pure, Se-doped and Te-doped SrTiO$_3$ are shown respectively, in Fig. 5a, b. The optical properties are obtained in the random-phase approximation (RPA), with a Drude-like shape for the intra-band contribution (Ambrosch-Draxl and Sofo 2006). The underestimation of band gap energy $E_g$ affects the optical absorption spectra form. To remediate this
shortcoming of GGA approximation, we applied an energy shifting of 1.35 eV (Scissors operator = E_g(experimental) − E_g(theoretical)) when calculating the optical properties.

As showed in Fig. 5a, The curve ε(ω) exhibits threshold energy arising at 3.15 eV for pure SrTiO_3. This energy corresponding to the band edge that may have originated from the electron transitions between the occupied O 2p states in the VBM and the unoccupied Ti 3d states in the VBM. The threshold energy shifts significantly to low energy, when we substitute O by S, and further shifts when we substitute O by Te, due to decreased band gap values. This shifting indicates a response expansion of SrTiO_3 to visible light region, as interesting region to explore for photocatalytic applications. These results are similar to experimental results about the effect of Se and Te doping in TiO_2 (Rockafellow et al. 2010; Mathew et al. 2020).

In the Fig. 5b, the spectrum of pure SrTiO_3 clearly shows the limited response of SrTiO_3 in the ultra violet light region, due to its large band gap. After doping, the absorption edge shifts to higher wave length of 447.65 nm and 587.68 nm for respectively, Se-doping and Te-doping cases, signifying enhancement in the visible absorptive ability for these systems, which might improve the photocatalytic performance of SrTiO_3. The obtained shifts of absorption edges to higher wavelengths correspond to the narrowing of band gaps after doping. We remark that the response of SrTiO_3 to visible light increases more with Te doping than with Se doping.

### 3.4 Photocatalytic properties

In photocatalytic water splitting process a heterogeneous semiconductor material is used as photocatalyst. Under illumination, the photons absorbed into the semiconductor (suspended in water) can excite electrons in the valence band (VB) into the conduction band (CB) leaving excited holes in the VB. The photogenerated electron–hole pairs then migrate to the surface of the photo-catalyst, and initiate the oxydo-reduction reactions with adsorbed water molecules in the active sites. This leads to obtain the dihydrogen H_2 and di-oxygen O_2, simultaneously, according to the following equations:

\[ H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2 \]  \hspace{1cm} (3)

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (4)
Equations (3) and (4) express the half equation for oxidation and reduction, respectively. The Eq. (5) gives the overall equation for water splitting.

For the photogenerated electron—hole pairs to be used for water splitting reaction, the CBM potential should be more negative than the reduction potential of $H^+/H_2$ ($0 \text{ eV vs. normal hydrogen electrode NHE}$), and the VBM potential should be more positive than the oxidation potential of $O_2/H_2O$ ($1.23 \text{ eV vs. normal hydrogen electrode NHE}$) as it is illustrated in Fig. 6a. Therefore, photocatalyst must be a semiconductor with band gap energy more than 1.23 eV, and its CBM and VBM must sandwich the water redox levels, to be used for water splitting.

To verify that the above conditions are met, we calculated the CBM and VBM potentials for all systems using the formulas (Wang et al. 2017):

$$E_{\text{CBM}} = -\frac{1}{2}E_g + \chi + E_0$$
$$E_{\text{VBM}} = E_g + E_{\text{CBM}}$$

where $E_0 = -4.5 \text{ eV}$ is the energy level of the normal hydrogen electrode (NHE) below the zero vacuum energy level, $E_g$ is the band gap energy, $\chi$ is the absolute electronegativity of system calculated by the formulas:

$$\chi_{\text{SrTiO}_3} = \left(\chi_{\text{Sr}}\chi_{\text{Ti}}\chi_{\text{O}}^2\right)^{\frac{1}{3}}$$
$$\chi_{\text{SrTiO}_{3-x}\text{M}_x} = \left(\chi_{\text{Sr}}\chi_{\text{Ti}}\chi_{\text{O}}^{3-x}\chi_{\text{M}}^x\right)^{\frac{1}{3}}$$

where $\chi_{\text{SrTiO}_3}$ the absolute electronegativity of pure SrTiO$_3$, $\chi_{\text{SrTiO}_{3-x}\text{M}_x}$ the absolute electronegativity of M-doped SrTiO$_3$ system (M = Se, Te and $x = 0.125$ for one M atom substitutes for one O atom), $\chi_{\text{Sr}}$, $\chi_{\text{Ti}}$, $\chi_{\text{O}}$ and $\chi_{\text{M}}$ are the absolute electro-negativities of Sr, Ti, O and M elements, respectively. According to the study of Bartolotti (Bartolotti 1987): $\chi_{\text{Sr}} = 1.75$, $\chi_{\text{Ti}} = 3.05$, $\chi_{\text{O}} = 8.92$, $\chi_{\text{Se}} = 5.91$ and $\chi_{\text{Te}} = 5.35$.

The calculated CBM and VBM positions vs. NHE at pH = 0 for all systems are summarized in Table 2, and their corresponding alignments are plotted in Fig. 6b.
It is demonstrated that the CBM and VBM for the pure SrTiO₃ straddle the water redox potentials, which means that water can be split into H₂ and O₂ by pure SrTiO₃. Besides the calculated CBM potential of pure SrTiO₃ is 0.88 eV, which is in line with the experimental result of Xu and Schoonen (2000). Figure 6b also shows that the CBM is significantly shifted in the downward direction due to doping with Se, and further shifted in the same direction due to doping with Te. This means that photo-reduction ability is improved. Besides, the VBM is shifted upward by Se doping and further shifted upward by Te doping, leading to photo-oxidation capacity improvement. Moreover, the CBM positions of doped systems are above the hydrogen reduction level and their VBM positions are bellow the water oxidation level. Consequently, water can be decomposed into H₂ and O₂ for doped systems.

Besides, the absence of isolated states in the forbidden band, and the good absorptive ability in the visible region for these systems, make them a part of promising materials for H₂ production by photocatalytic water splitting. This positive effect of selenium and tellurium on the optical and photocatalytic properties of SrTiO₃ is similar to the effect revealed experimentally in Se-doped TiO₂ (Xie et al. 2018; Rockafellow et al. 2010), Te-doped TiO₂ (Mathew et al. 2020) and S-doped SrTiO₃ (Le et al. 2016). The comparison between the two doped systems indicates that Te-doped SrTiO₃ has the more suitable band gap energy, absorptive ability and band edges levels for producing hydrogen from photo-catalytic water splitting.

**4 Conclusion**

In summary, compared to the undoped SrTiO₃, the Te and Se doping can reduce the width of bandgap significantly. The increase of covalency strength of Ti–O bond and the decrease of iconicity strength of Sr–O bond through doping Se and Te atoms in O site may be the origin of observed band gap narrowing. Both the Se doping and Te doping enhance the absorption of SrTiO₃ in the visible light region. But the Te doping enhanced more effectively the optical absorption in the visible light region and strengthen the red-shift, which is likely due to the higher covalency strength of Ti–Te bond in Te-doped SrTiO₃ compared to the covalency strength of Ti–Se in Se-doped SrTiO₃. The narrowed band gaps are free from any isolated states, which expected to help in inhibiting the faster recombination of photogenerated carriers and consequently improve the photocatalytic performance. The potentials of the CBMs and VBMs satisfy the thermodynamic requirements to trigger the water splitting reaction. Hence we suggest that the doping of Se and Te (particularly Te) into the SrTiO₃ material is one of the better choices to improve the yield for photosplitting of water under visible light.
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