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The effect of oxygen vacancies on water wettability of transition metal based SrTiO₃ and rare-earth based Lu₂O₃†

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Understanding the structural, physical and chemical properties of the surface and interfaces of different metal-oxides and their possible applications in photo-catalysis and biology is a very important emerging research field. Motivated in this direction, this article would enable understanding of how different fluids, particularly water, interact with oxide surfaces. We have studied the water contact angle of 3d transition metal oxide thin films of SrTiO₃, and of 4f rare-earth oxide thin films of Lu₂O₃. These metal oxides were grown using pulsed laser deposition and they are atomically flat and with known orientation and explicitly characterized for their structure and composition. Further study was done on the effects of oxygen vacancies on the water contact angle of the 3d and 4f oxides. For 3d SrTiO₃ oxide with oxygen vacancies, we have observed an increase in hydroxylation with consequent increase of wettability which is in line with the previous reports whereas an interesting opposite trend was seen in the case of rare-earth Lu₂O₃ oxide. Density functional theory simulations of water interaction on the above mentioned systems have also been presented to further substantiate our experimental findings.

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Introduction

Metal oxides comprise a diverse class of materials with intriguing properties and vital technological utility. Controlling and/or altering the interface between liquid ('water' specifically) and metal oxide surfaces, which is termed as "wetting", is of immense scientific interest. Understanding the underlying phenomena of wetting at the molecular level in such material systems is crucial for numerous technological processes. Among these metal oxides, reversible tunability of water wetting has been extensively studied in systems such as TiO₂ (ref. 1) and ZnO.²⁻⁵ Reversible wettability

and enhancement of hydrophilicity in metal oxide systems have been obtained through ultra violet (UV) illumination,^{5,6} visible light,⁷ electro-wetting,⁸ structural modifications,^{9,10} thermal treatment¹¹ and laser irradiation.¹² Detailed studies have been done to understand the underlying mechanism for enhancement in hydrophilicity in transition metal oxides for *e.g.* ZnO and TiO₂ and the plausible reasons that have been reported for this consequence are removal of organic contaminants,¹³ transition of crystal structure,¹⁴ increase of surface roughness,¹⁵ change of surface chemical compositions/hydroxyl content, oxygen vacancies and Ti³⁺ or Zn⁺ defect sites.¹⁶ In particular, modifications in wetting through changes in the electronic structure of transition metal oxides due to defect formation have gained attention over the past several years.^{1,3,4,12,17} Such modifications have been demonstrated through UV irradiation and photo-induced hydrophilicity has been observed for TiO₂, SnO₂, ZnO, WO₃, V₂O₅.¹⁸⁻²² The dissociation of water molecules into H and OH at vacancies sites of TiO₂ have been imaged through non-contact AFM and STM.²³⁻²⁶ SrTiO₃ whose electronic structure resembles TiO₂ does not exhibit photo-induced hydrophilicity under UV light, clearly indicates that wetting properties depend intimately on surface electronic structure, and not solely stoichiometry or surface roughness.²⁷

The increase in interactions of water with the surface defect sites have been well documented in the case of TiO₂ and ZnO but the effect of oxygen vacancies on the 4f element based metal oxides remains largely unexplored except a recent study on CeO₂.²⁸ In this article we have studied the wettability of pulsed

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laser deposition (PLD) grown rare-earth Lu_2O_3 oxide, with oxygen vacancies and have also investigated the effect of vacancy healing in such systems. In order to understand the underlying mechanism and also to make a comparison, commercially available SrTiO_3 substrates were studied by creating oxygen vacancies through thermal annealing. An opposite trend (in terms of how wettability varies with oxygen vacancy) has been observed in the case of these 3d and 4f oxides and this is in accordance with the density functional theory (DFT) calculations performed for such systems.

Experimental and computational methods

The macro scale contact angle measurements were carried out using the video based fully automated Data Physics optical contact angle microliter dosing system (OCA 40 Micro). Di water drops (1 μl per drop) with known surface tension (72.80 N m^{-1}) were dispensed using Teflon coated motor driven syringe. The contact angles were measured at ambient conditions and a video was recorded (72 frames per second) for every dispensed solvent droplet. Any dynamic changes to the droplet on the surface can be precisely observed through this method. The contact angle was estimated using the sessile drop technique by measuring the angle between the tangent lines along solid-liquid interface and liquid-vapour interface of the liquid contour as shown in Fig. 1. A contact angle of 0° and 180° correspond to complete wetting and non-wetting respectively. Surfaces exhibiting contact angles below 90° are called hydrophilic and those above 90° are called hydrophobic.

The SrTiO_3 samples were commercially available high quality single crystal substrates from CrysTec GmbH. The Lu_2O_3 thin films were deposited on YSZ [1 0 0] substrates by pulsed laser deposition using a stoichiometric target of Lu_2O_3 . YSZ [1 0 0] was chosen due to its similar cubic structure of intended Lu_2O_3 [1 0 0] phase and similar lattice parameter of 5.14 \AA whereas Lu_2O_3 [1 0 0] also has a lattice parameter of 11.03 \AA . Lu_2O_3 target was synthesized by a conventional solid state reaction. The starting materials for a target were high purity (99.995% or higher) powders of Lu_2O_3 . First, the powders were mixed for several hours manually using mortar and pestle. It was pressed into a 1 in. diameter die by hand press and then further pressed under 120 MPa for 30 min by cold isostatic pressure. It was then sintered at 1300 $^\circ\text{C}$ inside the tube furnace for 15 h under the steady flow of oxygen gas. The sintered target were examined by X-ray diffraction using laboratory powder X-ray source.

The thin films were deposited at a temperature of 850 $^\circ\text{C}$ and at 10 mTorr oxygen partial pressure. Before growth chamber

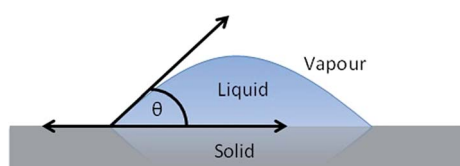


Fig. 1 Schematic diagram of a liquid drop on a solid surface showing contact angle θ .

was pumped down to base pressure of $\approx 5 \times 10^{-7}$ mbar. The 248 nm wavelength KrF laser was utilized to ablate the ceramic target. The incident laser energy density and the repetition rate were 1.5 J cm^{-2} and 5 Hz, respectively. The crystal structure and phase of the thin films were examined by X-ray diffraction (Bruker D8 Advanced Thin Film XRD).

We employed density functional theory (DFT) calculations to gain insights into the properties of surface oxygen vacancies and their interaction with water. We have included a Hubbard U term on the Lu f states ($U_{\text{eff}} = 5.4$ eV)²⁹ and Ti d states ($U_{\text{eff}} = 3.0$ eV).³⁰ For SrTiO_3 , where formally the Ti electronic configuration is d^0 , we have verified that the reported energetics depend only slightly on the inclusion of the U term by comparing the results with pure DFT.

We considered the TiO_2 -terminated (001) surface of SrTiO_3 as it is expected to be the exposed surface of commercially available SrTiO_3 . For Lu_2O_3 the [100] orientation of cubic bixbyite is polar, so we can expect some extent of reconstruction to compensate polarity. As a simplified model of a compensated nonpolar surface we have considered the (0001) surface of hexagonal Lu_2O_3 . The surfaces were represented with slab of 10 and 12 \AA thickness for Lu_2O_3 and SrTiO_3 , respectively, where for SrTiO_3 we used a symmetric non-stoichiometric slab. The concentration of oxygen vacancies and/or water molecules was set to 1/4 ML, by using a surface (2×2) unit cell. The water adsorption energy was computed with respect to a water molecule in the gas phase: $E_{\text{ads}} = E(^*\text{H}_2\text{O}) - E(^*) - E(\text{H}_2\text{O})$, where $E(^*\text{H}_2\text{O})$, $E(^*)$ and $E(\text{H}_2\text{O})$ are the total energies of an adsorbed water, the surface, and the gas phase water molecule, respectively. All atomic positions except the bottom oxide layer were fully relaxed until the forces on each atom were below 0.01 eV \AA^{-1} . All calculations were performed within the PBE functional³¹ as implemented in the VASP code.³²

Results and discussion

This study mainly reports morphological, structural and wettability behaviours of SrTiO_3 and Lu_2O_3 sample surfaces before and after annealing.

For SrTiO_3 , high quality single crystal substrates are bought from Crystec, GmbH, Germany and the as received substrate goes through a 6 hour annealing step at 900 $^\circ\text{C}$ at a very low pressure of 10^{-6} Torr. The experiment is performed inside a Pulsed Laser Deposition (PLD) chamber. This annealing step was done to create significant amount of oxygen vacancies in the SrTiO_3 single crystal sample.

For Lu_2O_3 , these REO thin films were grown at low pressure (10 mTorr), so from the beginning they have significant amount of oxygen vacancies in them. In this case the annealing process was significantly different from the previous (SrTiO_3) one, here pristine Lu_2O_3 thin-films were annealed under atmospheric pressure at 900 $^\circ\text{C}$ for 6 hours inside a PLD chamber. Here the annealing process actually reduces oxygen vacancies instead of creating ones.

To rule out trivial (like hydrocarbon desorption) effect of annealing on water contact angle (WCA) we have waited long enough (more than 120 hours) before measuring the wettability data.



However, before making any comparative study in the field of water contact angle one must make sure that morphological and structural parameters are all similar in the samples before and after annealing procedure. In this direction we have done Atomic Force Microscopy (AFM) and X-ray diffraction (XRD) study for quantification of the morphological and structural parameters, respectively.

In Fig. 2 we have shown the root mean square (rms) surface roughness value of the Lu_2O_3 thin-film and SrTiO_3 single crystal samples using AFM (Agilent – 5500). Study of surface roughness is very important as it has been shown and well accepted that wettability is characterized by not only the chemical composition but also the roughness of the surface.³³ To rule out the effect of

surface roughness we have shown the surface roughness value of pristine and annealed samples. In case of Lu_2O_3 thin-film samples the R_{rms} values are very similar to each other, varying from 0.22 nm [Fig. 2(a)] to 0.53 nm [Fig. 2(b)] before and after annealing respectively. Similarly the surface roughness of TiO_2 terminated SrTiO_3 single crystal varies from 0.15 nm [Fig. 2(c)] to 3.01 nm [Fig. 2(d)] before and after annealing respectively. In TiO_2 terminated SrTiO_3 single crystal samples AFM images of the pristine samples [Fig. 2(c)] clearly showing the atomic step-edges which is gone after high pressure annealing [Fig. 2(d)]. Value of all this surface roughness is very low, all of them are below 5 nm for both SrTiO_3 single crystal and Lu_2O_3 thin-film samples. This

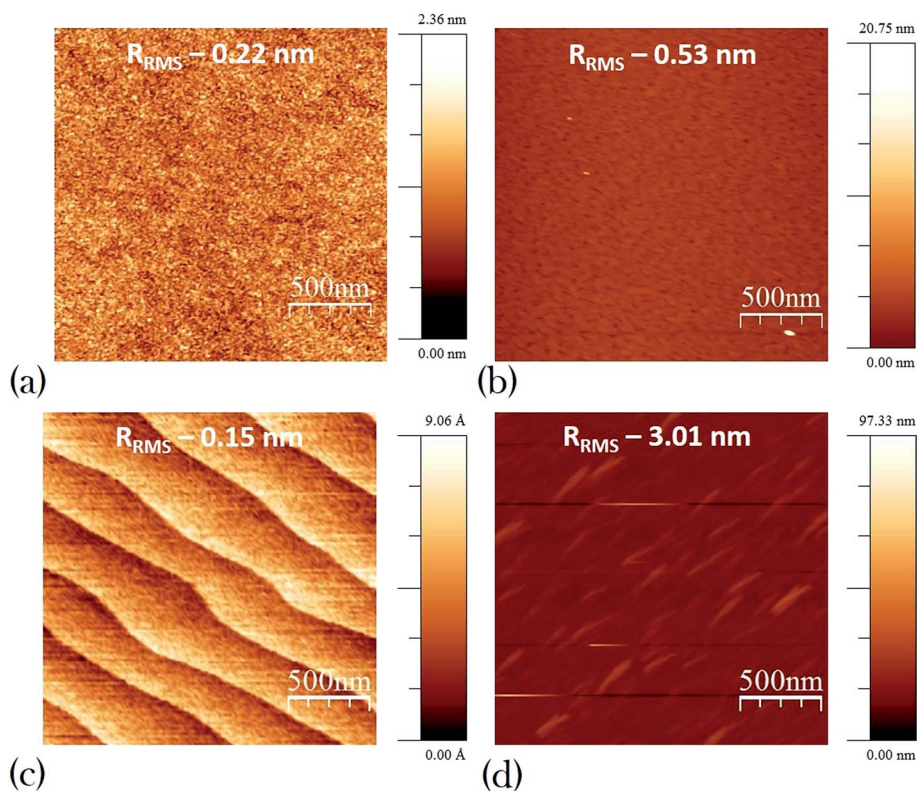


Fig. 2 Atomic force microscopy (AFM) images of Lu_2O_3 (a) pristine (b) annealed and TiO_2 terminated STO (c) pristine (d) annealed.

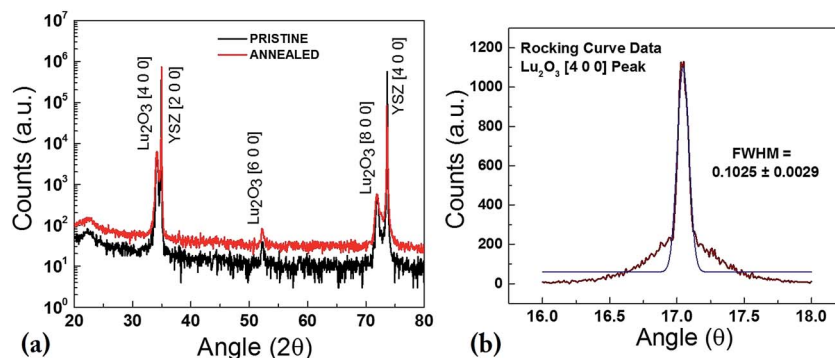


Fig. 3 XRD study – (a) $\theta-2\theta$ scan of pristine and annealed Lu_2O_3 showing no structural change upon annealing; (b) rocking curve measurement of annealed Lu_2O_3 [4 0 0] peak showing high quality thin-films used in the study.



amount of morphological change cannot explain the significant change we observe in WCA value.

XRD technique was used to study the effect of annealing on the structural properties of these thin-films and substrates. PLD grown Lu_2O_3 thin films were studied using Bruker D8 Advanced Thin Film XRD. Fig. 3(a) shows the theta-2 theta scan of the pristine Lu_2O_3 thin-films grown at 800°C at 100 mTorr oxygen partial pressure and annealed Lu_2O_3 thin-films in red and blue lines respectively. As shown in the images all thin-films are phase pure and Lu_2O_3 films grows along $[1\ 0\ 0]$ direction. First XRD peak for Lu_2O_3 is found at 34.1° for $[4\ 0\ 0]$ peak and two subsequent peaks of Lu_2O_3 $[6\ 0\ 0]$ and $[8\ 0\ 0]$ are found at 52.2° and 71.9° respectively, along with two substrate peaks of YSZ $[2\ 0\ 0]$ & $[4\ 0\ 0]$ at 34.9° and 73.5° . The careful study at Fig. 3(a) reveals that the XRD pattern and peak location of both pristine and annealed thin-films are identical. The Lu_2O_3 thin-films are grown at 800°C and it was not expected that annealing at 900°C would create any significant structural changes in the highly stable cubic crystal structure of Lu_2O_3 $[1\ 0\ 0]$ phase with lattice parameter of $11.03\ \text{\AA}$. Additional rocking curve data of annealed Lu_2O_3 $[4\ 0\ 0]$ also suggests very good quality thin-film sample with a FWHM of 0.103° . SrTiO_3 samples were single crystal substrates which eliminates any need of XRD analysis before and after annealing.

Further study was done for the quantification of the oxygen vacancy in the samples, as shown in the Fig. 4. In case of Lu_2O_3 we have used Rutherford Back Scattering (RBS) method to show that relative presence of elemental oxygen increases with the annealing step. For RBS study Lu_2O_3 thin-films samples grown on Si $(1\ 0\ 0)$ was used, as it is not possible to find precise determination of oxygen atomic content when substrate is a another oxide like YSZ. The Lu_2O_3 thin-films grown on Si also goes through exactly similar growth and annealing condition like the Lu_2O_3 $(1\ 0\ 0)$ grown on YSZ $(1\ 0\ 0)$. In Fig. 4(a) and (b) as we see elemental analysis using RBS reveals that Lu : O ratio is $0.44 : 0.56$, whereas after the oxygen annealing the elemental composition ratio of Lu : O becomes $0.41 : 0.59$, a clear increase of oxygen content and in the latter case the Lu : O ratio approaches the ideal elemental ratio of $0.40 : 0.60$ in case of Lu_2O_3 . RBS technique is clearly showing all the silicon, oxygen and lutetium edges in the spectra. [Further support of enhanced presence of relative oxygen can be achieved using XPS data

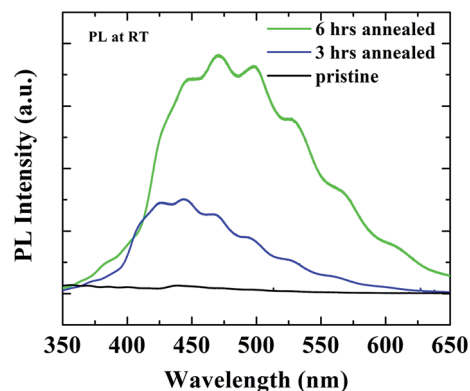


Fig. 5 Photoluminescence of as-received and annealed SrTiO_3 single crystal substrate.

which shows clear increment of the O 1s to Lu 4d ratio (O 1s : Lu 4d) with annealing, a result consistent with reduction of oxygen vacancies (see 'ESI' Fig. S1†).]

In the SrTiO_3 case RBS technique could not be used to assess oxygen vacancy content as for oxides with more than two elements it is difficult to decisively find out elemental composition at a very precise level, particularly when one element is low atomic number (oxygen) with very low Rutherford cross-section. As we have discussed above, the low oxygen partial pressure annealing should enhance amount of oxygen vacancies. To further detect the effect of annealing in the SrTiO_3 substrates photoluminescence (PL) was performed after annealing at room temperature. Fig. 5 shows that the intensity of the broad PL peak (position around $475\ \text{nm}$) of SrTiO_3 substrate increases monotonically with increasing annealing time. It has been previously reported that broad PL emission of SrTiO_3 in blue range (between 450 to $500\ \text{nm}$) dramatically increase with increasing oxygen vacancy in the SrTiO_3 .^{34–37} It has been theorized that oxygen vacancies in SrTiO_3 generate conduction carriers and stabilize a hole level in a self-trapped state and hence the doped conduction electrons and the in-gap state produce a radiative process that results in blue-light emission.³⁴ Also here in Fig. 5 we find a similar trend which clearly indicates that with increasing annealing time more oxygen vacancies are created in our SrTiO_3 substrates.

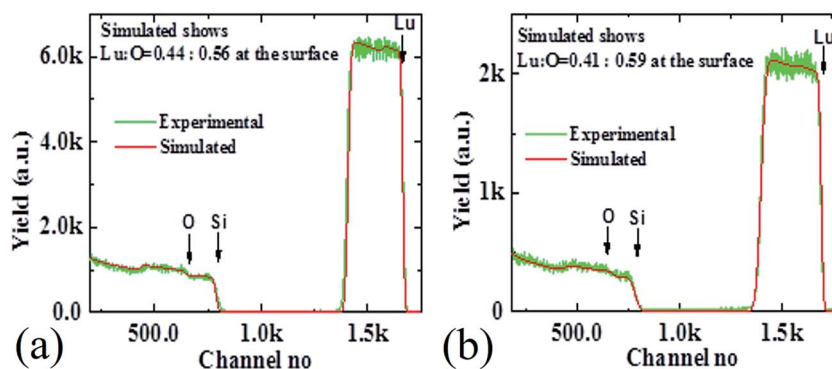


Fig. 4 Quantification of oxygen vacancy using RBS technique in (a) as-grown and (b) annealed Lu_2O_3 sample.



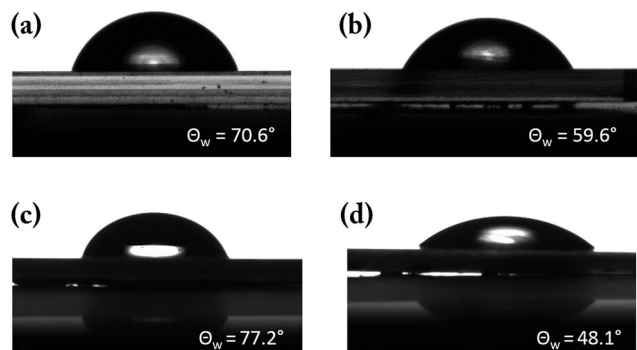


Fig. 6 Water contact angle obtained on Lu_2O_3 (a) pristine (b) annealed and SrTiO_3 (c) pristine (d) annealed.

Fig. 6 shows the contact angle measurement of Lu_2O_3 thin-films and SrTiO_3 single crystal before and after annealing. As shown in Fig. 6(a) the as-grown Lu_2O_3 thin-films sample showing a moderately high water contact angle (70.6°) before any annealing process, whereas following the annealing [Fig. 6(c)] water contact angle comes out to be much lower (59.6°). XPS spectra collected in the C 1s region (Fig. S2†) show no significant change upon annealing, suggesting that the change in contact angle is not due to the formation (or removal) of surface carbonates. A very similar behaviour of WCA upon annealing is also found on another REO thin-film system of CeO_2 [see 'ESI' Fig. S3 for the details†].

Subsequently in the lower panel of the Fig. 6, *i.e.* in Fig. 6(c) and (d) we have reported the water contact angle of as-received and annealed SrTiO_3 single crystal samples respectively. The

pristine SrTiO_3 single crystal samples shows high water contact angle (77.2°) compared to the annealed thin-films (48.1°).

Here we find an interesting contradictory behaviour in REO Lu_2O_3 (and CeO_2) thin film and SrTiO_3 single crystal samples: for SrTiO_3 , oxygen vacancy promotes wettability, while for Lu_2O_3 (and CeO_2) it is the opposite direction – oxygen vacancy hinders wettability.

Finally to understand the contradictory behaviour of water contact angle with the creation of oxygen vacancies in SrTiO_3 and Lu_2O_3 systems, we have used Density Functional Theory (DFT) calculations. Various configurations have been considered for the adsorption of water on the oxide surface in presence of an oxygen vacancy. In the case of the TiO_2 -terminated SrTiO_3 (001) surface we found that in the most stable configuration water adsorbs dissociatively at the vacancy site with an adsorption energy of -2.30 eV, to be compared to -0.74 and -0.98 eV of molecular and dissociative adsorption on the clean surface. In the dissociated configuration the oxygen of water heals the vacancy and the two hydrogen atoms form hydroxyl groups with surface oxygen atoms, Fig. 7(d). A similar mechanism has been already reported for TiO_2 and other oxides as discussed in the introduction. The polar hydroxyls groups created upon contact of the defective surface with water can form oxygen bonds with the subsequent water layers increasing the surface wettability.³⁸ Conversely, on the hexagonal Lu_2O_3 surface healing of oxygen vacancies with water is not energetically favourable and the most stable configuration consists of molecular water adsorbed on a Lu site adjacent to the vacancy (Fig. 6(b)), resulting in an adsorption energy of -0.74 eV (compared to -0.37 eV of the clean surface). This adsorption mode

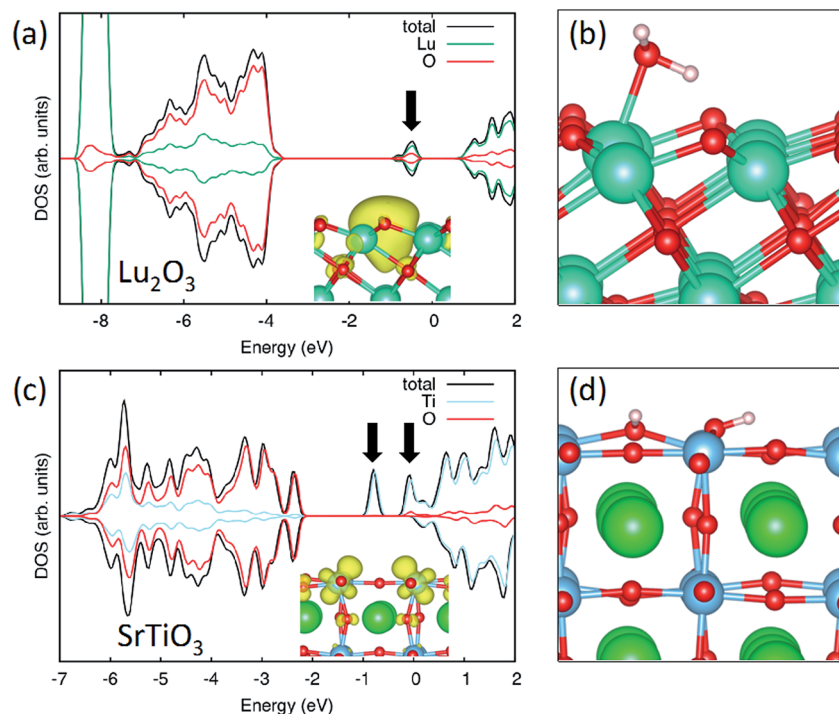


Fig. 7 Density of States (DOS) for a surface oxygen vacancy at the Lu_2O_3 (a) and SrTiO_3 (c). The insets show the electron density of the defect state, indicated by the arrows in the DOS. Most stable configurations for a water molecule at the surface of defective Lu_2O_3 (b) and SrTiO_3 (d). O atoms are represented in red, Lu in light green, Sr in green, Ti in blue and H in white.



does not create hydroxyls groups and thus does not enhance surface wetting in agreement with the contact angle measurements. The increased wetting observed experimentally for the pristine sample, Fig. 5, can be ascribed to OH species present on this sample, likely at low coordinated sites, which desorbs (being oxidized to leave a filled, unprotonated oxygen site only, desorbing as water) upon annealing. This interpretation is consistent with O 1s data, Fig. S1,† which show a higher OH signal for the pristine sample.

The difference between the two materials can be linked to the different nature of the oxygen vacancy on the two oxides. In the case of SrTiO₃ the vacancy formation reduces the Ti ions from +4 to +3 oxidation state (with a concentration of two Ti³⁺ per vacancy site), Fig. 7(c). When water is adsorbed the two extra-electrons remain in the Ti 3d states and the concentration of Ti³⁺ is maintained. This similarity between the electronic properties of O-deficient and hydroxylated surface has been already observed for TiO₂.³⁹

In the case of Lu₂O₃, the Lu f states are not accessible for reduction and the two electrons left in the material when a neutral oxygen vacancy is formed stay localized at the vacancy site Fig. 7(a). This state corresponds to a defect state in the band gap. When water is introduced, the adsorption at the vacancy site is hindered as the extra electrons cannot be accommodated at the metal sites (as the Lu states are too high in energy). As a consequence, the molecule stays at a metal site near the vacancy where it can benefit from electrostatic interaction with the trapped electrons.

We also note a correlation between the increased wetting at defective SrTiO₃ which is more conductive, compared to Lu₂O₃ which maintains its insulating nature.

Conclusion

In this article, we have reported the contradictory behaviour of water contact angle with oxygen defect creation in 3d transition metal based oxide SrTiO₃ and 4f rare-earth based Lu₂O₃ systems. In case of SrTiO₃ we find that oxygen vacancy promotes wettability, where as in case of Lu₂O₃ we find the effect of oxygen is exactly opposite, *i.e.* that oxygen vacancy inhibits wettability. Post growth annealing at either high or low oxygen partial pressure was used to remove or create oxygen vacancy in both Lu₂O₃ and SrTiO₃ samples respectively. We have used XRD and AFM measurement to rule out any possible role of structural and surface morphological change (with annealing) that can affect water contact angle. Further study was done using RBS and room temperature PL technique to demonstrate the change of oxygen vacancy level before and after annealing. Finally DFT calculations was used to conclude that in the case of SrTiO_{3-x} we expect an increase of hydroxylation compared to stoichiometric SrTiO₃ with a consequent increase of wettability, which effect is not present for Lu₂O₃.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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