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Decision letter and referee reports: first round

10th Feb 20

Dear Dr Ivanov,

Thank you for submitting your manuscript, "The effect of the oxygen vacancy ordering on the oxygen exchange kinetics in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of potential interest, all 3 referees have raised substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but would be interested in considering a revised version that addresses these concerns.

We hope you will find the referees' comments useful as you decide how to proceed. Should further experimental data or analysis allow you to address these criticisms, we would be happy to look at a substantially revised manuscript. However, please bear in mind that we will be reluctant to approach the referees again in the absence of major revisions. If the revision process takes significantly longer than three months, we will be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A rebuttal letter with a point-by-point response to each of the referee comments and a description of changes made. Please include the complete referee report in the rebuttal letter. Please note that the rebuttal letter must be separate to the cover letter to the editors.

-A marked-up version of the manuscript with all changes to the text in red colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

-A clean version of the manuscript. Please select the file type 'Article File'.

-An updated <https://www.nature.com/documents/nr-editorial-policy-checklist.pdf> Editorial Policy checklist, uploaded as a 'Related Manuscript File' type. This checklist is to ensure your paper complies with all relevant editorial policies. If needed, please revise your manuscript in response to these points. Please note that this form is a dynamic 'smart pdf' and must therefore be downloaded and completed in Adobe Reader, instead of opening it in a web browser.

Please use the following link to submit your revised manuscript files:

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**** This url links to your confidential home page and associated information about manuscripts you may have submitted or be reviewing for us. If you wish to forward this email to co-authors, please delete the link to your homepage first ****

Please do not hesitate to contact me if you have any questions or would like to discuss the required revisions further. Thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD

Chief Editor

orcid.org/0000-0003-4824-8497

Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Please see the attached file.

Reviewer #2 (Remarks to the Author):

In this paper the authors have prepared thin films of LSC perovskite deposited on STO or LAO substrates in an effort to induce either compressive or tensile strain. They then use microscopy and isotopic exchange to study the oxygen transport characteristics of these films and correlate differences in the transport with structural changes, suggesting that a brownmillerite phase is formed in one case.

Much of the case is made through interpretation of the TEM data using the GPA methods, with modulation ascribed to oxygen ordering. As the interpretation of subtle features in the GPA data are central to this paper it is disappointing that further details of the method employed are not included. I also find it surprising that some details of the film quality, thickness etc are not provided. What thickness film is deposited? Is the strain state maintained throughout the film, or only close to the interface with the substrate? Assuming that there is a strain gradient away from the interface, would this affect the interpretation of the diffusion data?

Additionally the preparation of the trench in the film using the FIB has been known to induce amorphisation of the film edges. Have the authors verified that there is no damage induced by the FIB milling, and that this does not have an effect on the surface exchange coefficients measured?

There are also questions regarding the exchange experiments. The oxygen 16 anneal and the oxygen 18 anneal are both of 1 hour duration. Normally an oxygen 16 anneal is undertaken for significantly longer than the exchange anneal to ensure that the material is equilibrated, and has little to do with the background oxygen 18 concentration, other than to ensure absolutely that all measured oxygen 18 is from the exchange anneal. This is critical to ensure that a self diffusion experiment is performed and that there is no chemical diffusion. Can the authors confirm that they have verified that their exchange conditions have not induced any chemical diffusion?

Also, the surface exchange data plotted in Figure 4 suggest a difference of 30-60 times between strain states. Does this range include the maximum extent of the experimental uncertainties plotted?

It would also be useful to compare how these strained data compare with bulk materials - is there any variation away from bulk properties. If there is that would surely strengthen the argument regarding the structural influence.

Overall this is an interesting paper with useful new data, but there are some significant areas where there could be improvements made.

Reviewer #3 (Remarks to the Author):

Report on "The effect of oxygen vacancies on the oxygen exchange kinetics in La_{0.6}Sr_{0.4}CoO_{3-d} thin films" by Ivanov et al.

Dear Editor,

The authors report an study of oxygen diffusion in LSCO (x=0.4) thin films under different degrees of epitaxial strain. The surface exchange coefficient, k^* , and diffusion coefficient, D^* , were determined by ¹⁸O-isotope exchange ToF-SIMS experiments.

The authors found important differences in oxygen diffusion between both types of films, with both diffusion and exchange increasing substantially with tensile strain.

A microstructural study reveals that the concentration of O-vacancies is larger in the tensile-strained thin film, which transforms into a brownmillerite (BM) phase.

My main criticism to the paper is about its novelty. Some of the authors published a paper in ACS Nano 3276 (2013) with a very similar study on similar samples (over similar substrates) in which both k^* and D^* were studied by ToF-SIMS to conclude that "much faster surface exchange (4 times) and diffusion (10 times) were observed for the tensile strained films compared to the compressively strained films in the entire temperature range". This is basically the same conclusion as here.

From this point of view, only the link between the increase of k^* and D^* with tensile strain and the formation of the BM phase could be considered as an original contribution. However, the formation of the BM is also well known in these oxides and the effect of strain well documented (ref. 28, 29, and many more in the recent literature).

On the other hand, the discussion of some parts (results) is very poor. For instance, the differences between D^* and k^* with literature values are only mentioned but deserve a much deeper discussion. Also, the discussion of the EELS data is rather limited and the justification of the high/low spin state of Co is completely speculative, without any evidence from their data to support it. Sentences like "the high spin state of Co₂rows in the brownmillerite phase could additionally contribute to the observed difference in the oxide ion diffusion kinetics", need, at least, an explanation. How do the authors think this could happen? Are they proposing a change in the hybridization of Co-O bond so the formation/mobility of O-vacancies changes with the spin state, or it is only related to a volume effect? How would this impact anisotropic O-diffusion/exchange?

In summary, I do not think this paper adds anything useful to the literature of oxygen diffusion in Co oxides, and therefore I cannot recommend its publication.

Title: The effect of the oxygen vacancy ordering on the oxygen exchange kinetics in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films

Authors: Yu.P. Ivanov, M. Kubicek, H. Hutter, J. Fleig, A. Chuvilin, Z. L. Zhang

The manuscript is unacceptable in its present form but is a publishable subject with major revisions noted.

Comments:

The effect of epitaxial strain on oxygen diffusion and surface exchange is an important subject to the materials research community. In this manuscript, the authors fabricated $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) thin films on two different substrates, SrTiO_3 (STO) and LaAlO_3 (LAO). Due to the lattice mismatch between the film and the substrates, STO and LAO introduced tensile and compressive strain, respectively, into the LSC films. Using ToF-SIMS, TEM, EELS and GPA, the authors reported how strain can influence the oxygen transport and surface exchange kinetics of LSC films, correlating the oxygen vacancy ordering induced by strain. However, several key information are missing to support the authors' argument on the effect of the strain-induced vacancy ordering on oxygen transport and surface exchange kinetics. There are also discrepancies in the provided data. There are some grammatical errors and typos as well.

1. In the manuscript, the authors mainly discussed the relationship between the oxygen transport and the strain-induced vacancy ordering. Indeed, the aim of this manuscript is to investigate the structural reasons of oxygen transport enhancement associated with strain at the atomic level according to the authors. However, the title of this manuscript is “the effect of the oxygen vacancy ordering on the oxygen exchange kinetics in LSC thin films”. The authors are suggested to change either the title or the discussion direction in the manuscript.

2. The dark stripes caused by oxygen vacancy ordering and the formation of ordered superstructures by vacancy ordering have been intensively studied in the case of LCO and LSCO thin films. The authors should refer to the previous works in the introduction.

3. page 3, the authors mentioned “effect” many times (e.g., different possible effects....., different effects of the same strain....., experimental deconvolution of individual strain effects.....). The authors should clarify the effects on what.

4. page 3, the authors argued there have been no attempt for experimental deconvolution of strain effects. However, to the best of the reviewer’s knowledge, the authors can find many journal references about an experimental deconvolution of strain effects on transport/oxygen exchange /ferromagnetic/vacancy formation/ion migration/etc.

5. page 3, the authors mentioned that our observations reveal the epitaxial growth of LSCO on LaAlO_3 (LAO) substrate with small out of plane tensile stress of about 3% and pronounced oxygen vacancies ordering in Brownmillerite phase of LSCO growing on the SrTiO_3 (STO) substrate. In the thin film society, 3% strain is considered as a huge strain state. In addition, the authors reported

the out of plane expansion is smaller than expected for the compressed bulk. How did the authors conclude “LSCO on LaAlO₃ (LAO) substrate with small out of plane tensile stress of about 3%”? In addition, strain is a more appropriate term rather than stress in epitaxial thin films.

6. page 4, The authors should include the out-of-plane X-ray diffraction results of tensile and compressive strained LSCO films. In addition, the authors used STO and LAO substrates to grow LSCO films. Then, it should be easy to measure the reciprocal space maps (RSM) of the samples to clearly determine whether LSCO films are strained or not. The authors are suggested to include the RSM data as well. Accordingly, the authors also need to add the experimental details of the XRD and RSM.

7. page 8, the determination of the diffusion coefficient is not hampered by these surface effects, Sr segregation. However, the strained films used in this study may have the surface Sr segregation depending on the strain state and/or the quality of the films. This will influence the oxygen surface exchange kinetics. Did the authors confirm no Sr segregation or no discernible surface difference in the films used?

8. page 10, The authors mentioned that it was not possible to find a suitable temperature for exact determining D^* of both strain states for the reasons described there⁹. The authors are suggested to state more details of the reasons described in the reference.

9. page 12, Fig 6. What is the direction of the vacancy ordering in LSCO/LAO? As the authors pointed out, it is believed that oxygen vacancies can increase the unit cell volume of LSCO. In Fig 6e, the authors estimated the volume of the bulk LSCO assuming a simple elastic model. If this estimation is correct, this data represents more oxygen vacancies in the bulk LSCO compared to the compressive strained LSCO film. How is the volume of the bulk LSCO without any modulation? Is it still larger than that of LSCO/LAO films?

10. page 13, In Fig 7e, the volume of the LSCO/STO film is similar to that of the expanded bulk LSCO. Does this data represent both the LSCO/STO film and the bulk LSCO have a similar level of oxygen vacancies? In Fig 7a, the authors showed the magnified HAADF image showing the formation of BM phase. It is good to add the magnified HAADF image showing the BM phase in the LSCO/LAO in Fig 6.

11. page 16, In Fig. 8, the authors compared EELS data of the LSCO/STO and LSCO/LAO. The authors argued that there is no pronounced difference between O-K edges collected from the different Co atomic rows for LSCO deposited on the LAO substrate in contrast to the LSCO/STO. However, the data show no pronounced difference between O-K edges collected from the different Co atomic rows for both LSCO/STO and LSCO/LAO as compared to the data in Ref. 28 and another reference (see PRL 112, 087202, 2014). The authors should rewrite their argument. If necessary, the authors are suggested to include more clear data about O-K edges.

12. page 17. The authors calculated the oxygen nonstoichiometry of the LSCO films based on their GPA data. However, GPA data only represents the localized area of the LSCO films. It cannot represent the overall feature of the LSCO films. The authors obtained 0.05 for the LSCO/LAO and 0.22 for the LSCO/STO films. Considering the typical δ values of the bulk LSCO (0.01 – 0.02), the reviewer cannot trust the obtained δ values for the LSCO films. If the obtained δ values for the LSCO films are correct, how can the authors explain the volume comparison in Fig. 6 and 7 based on the obtained δ values?

13. In general, the k^* and δ value of the bulk LSCO (Sr=0.4) are $\sim 4 \times 10^{-8}$ and 0.02, respectively ($\sim 550 - 650^\circ\text{C}$, 1atm). In this manuscript, the authors obtained the k^* of $\sim 1 \times 10^{-8}$ for the tensile strained LSCO that has δ of 0.22 and the k^* of $\sim 1 \times 10^{-10}$ for the tensile strained LSCO that has δ of 0.05. Then, δ seems to have no effect on the oxygen surface exchange kinetics for LSCO. The authors should provide clear and detailed explanations of it.

14. Overall, the authors argument that the role of oxygen vacancy ordering in transport and surface exchange kinetics for LSCO is not clear. For example, the authors only emphasized that all the properties of LSCO/STO (tensile strained film) are related to a BM like superstructure. It is known that the oxygen vacancy ordering in LSCO eventually forms a BM-like superstructure. What is the role of BM like superstructure in transport and surface exchange kinetics for the compressive strained LSCO films? In addition, the authors did not provide any theoretical prediction of the formation energy of oxygen vacancies. But, the authors claimed that in their conclusion. Where is it from?

Author rebuttal letter: first round

Point-by-point response sheet

Reviewer 1

Comments: The effect of epitaxial strain on oxygen diffusion and surface exchange is an important subject to the materials research community. In this manuscript, the authors fabricated $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) thin films on two different substrates, SrTiO_3 (STO) and LaAlO_3 (LAO). Due to the lattice mismatch between the film and the substrates, STO and LAO introduced tensile and compressive strain, respectively, into the LSC films. Using ToF-SIMS, TEM, EELS and GPA, the authors reported how strain can influence the oxygen transport and surface exchange kinetics of LSC films, correlating the oxygen vacancy ordering induced by strain. However, several key information are missing to support the authors' argument on the effect of the strain-induced vacancy ordering on oxygen transport and surface exchange kinetics. There are also discrepancies in the provided data. There are some grammatical errors and typos as well.

R: We thank Reviewer 1 for the insightful comments. In the revised version, we address his/her comments as stated below.

Q1: In the manuscript, the authors mainly discussed the relationship between the oxygen transport and the strain-induced vacancy ordering. Indeed, the aim of this manuscript is to investigate the structural reasons of oxygen transport enhancement associated with strain at the atomic level according to the authors. However, the title of this manuscript is “the effect of the oxygen vacancy ordering on the oxygen exchange kinetics in LSC thin films”. The authors are suggested to change either the title or the discussion direction in the manuscript.

R: We changed the title on “Strain induced structure and oxygen transport interactions investigated on epitaxial $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films”

Q2: The dark stripes caused by oxygen vacancy ordering and the formation of ordered superstructures by vacancy ordering have been intensively studied in the case of LCO and LSCO thin films. The authors should refer to the previous works in the introduction.

R: In the revised version the corresponding references were inserted also into the Introduction. We tried to address all literature sources including the most recent ones related to the formation of ordered superstructures in LSCO epitaxial films through the text as appropriate.

Q3: page 3, the authors mentioned “effect” many times (e.g., different possible effects...., different effects of the same strain...., experimental deconvolution of individual strain effects.....). The authors should clarify the effects on what.

R: The sentence was modified “An experimental deconvolution of individual local strain effects on the oxygen exchange kinetics with combined in-plane and across-plane diffusion experiments has not been attempted so far to the best of the authors' knowledge.”

Q4: page 3, the authors argued there have been no attempt for experimental deconvolution of strain effects. However, to the best of the reviewer's knowledge, the authors can find many

journal references about an experimental deconvolution of strain effects on transport/oxygen exchange /ferromagnetic/vacancy formation/ion migration/etc.

R: The aim of the current manuscript is to reveal the local atomic structure in epitaxial films macroscopically strained (tensile/compressive) due to the corresponding mismatch with the substrate and link it to the oxygen diffusion kinetics both in-plane and across-plane. This is the first attempt for the best of our knowledge. We clarify this point in the Introduction of the revised version of the manuscript.

Q5: page 3, the authors mentioned that our observations reveal the epitaxial growth of LSCO on LaAlO₃ (LAO) substrate with small out of plane tensile stress of about 3% and pronounced oxygen vacancies ordering in Brownmillerite phase of LSCO growing on the SrTiO₃ (STO) substrate. In the thin film society, 3% strain is considered as a huge strain state. In addition, the authors reported the out of plane expansion is smaller than expected for the compressed bulk. How did the authors conclude “LSCO on LaAlO₃ (LAO) substrate with small out of plane tensile stress of about 3%”? In addition, strain is a more appropriate term rather than stress in epitaxial thin films.

R: We emphasise two different structural cases observed for LSCO films epitaxially grown on STO and LAO substrates. Since the obvious lattice mismatch between substrate and LSCO, the epitaxial films should be strained. To estimate the strain originated from the substrate, we used the simple model based on the Poisson coefficient of bulk LSCO. On the other hand, it is known, the lattice parameter of the oxide perovskites is affected by an oxygen non-stoichiometry. The combination of those effects produces distinctly different local atomic structure for tensile and compressive strained LSCO.

As we demonstrated, the LSCO(40% Sr) epitaxial films almost fully accommodate the tensile strain from the STO substrate, the average out of plane and in-plane lattice parameters are similar to the STO. But locally (within neighboring atomic rows) we observed large difference in the both lattice parameters. It is similar to the previously reported so-called Brownmillerite phase of LSCO, superstructure with the modulated lattice parameter. Due to the oxygen vacancies ordering in the adjacent atomic planes, locally the lattice parameter oscillates with the period of 2 unit cells. Note, such atomic arrangement is typically favorable for higher doping level than in our case - 40 %.

For the compressive strained LSCO, our study shows the average in-plane lattice parameter is close to the value of the LAO substrate. But the average out-of plane lattice parameter is significantly large. The 3% is related to the difference between the lattice parameter of our LSCO film and LAO substrate in out of plane direction. It is expected from the simple Poisson model due to the compressive strain induced by LAO substrate. Actually, the expected value is supposed to be larger than found in our investigation. What is why we used “with small out of plane tensile stress of about 3%”. We clarified this statement in the revised version. Note, there is also local modulation of the out-of plane lattice parameter with 2 unit cells periodicity similar to the Brownmillerite phase, but the difference in lattice parameter is much smaller.

Overall the macroscopic strain from the substrate and oxygen non-stoichiometry (40% doped LSCO) produce complex and distinct picture of the local strain distributions for film grown on LAO and STO substrate.

Q6: page 4, The authors should include the out-of-plane X-ray diffraction results of tensile and compressive strained LSCO films. In addition, the authors used STO and LAO substrates to grow LSCO films. Then, it should be easy to measure the reciprocal space maps (RSM) of the samples to clearly determine whether LSCO films are strained or not. The authors are suggested to include the RSM data as well. Accordingly, the authors also need to add the experimental details of the XRD and RSM.

R: We have added XRD-RSM study as requested by the reviewer. The new Figure 6 shows X-ray diffraction (XRD) in Bragg-Brentano geometry and X-ray reciprocal space mapping (RSM) on LSCO thin films deposited on LAO and STO substrates. Only {001} type diffraction peaks of LSCO are observed. The good quality of the 20 nm epitaxial thin films is shown by the visible Kiessig fringes on the inserts of the Figure 6a,b. From RMS study the thin film peaks are broader for LSCO/LAO film.

Accordingly, we added the new text to the experimental section. And there are two more co-authors included Matthäus Siebenhofer and Alexander Viernstein who did the measurements & evaluation of the data.

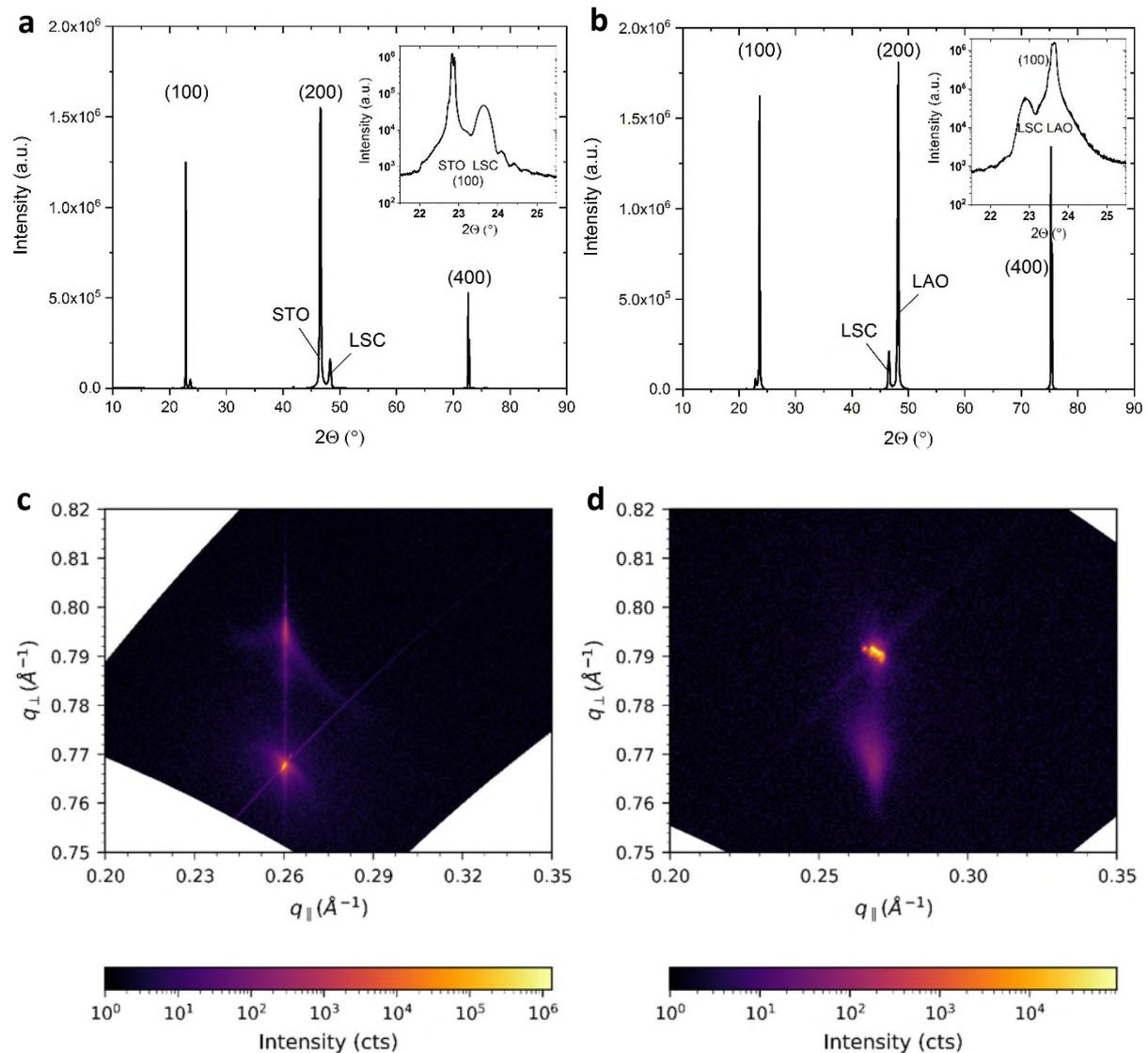
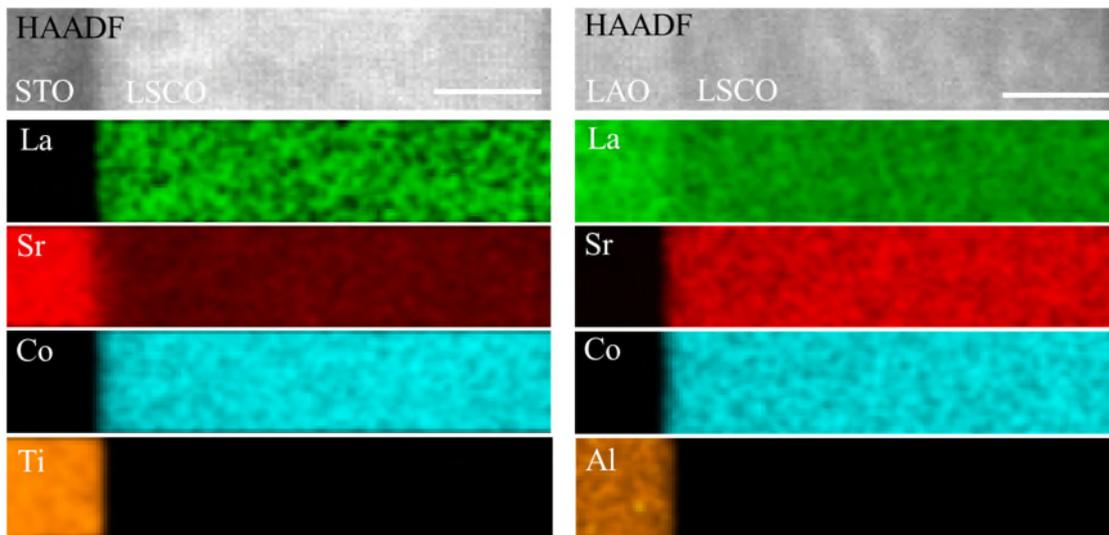


Figure 6. XRD-RSM study. θ -2 θ scans of (a) LSCO/STO and (b) LSCO/LAO show only {100} diffraction peaks of LSCO. The inset shows a magnification of the 001 peaks. The good quality of the 20 nm epitaxial thin films is shown by the visible Kiessig fringes. X-ray diffraction reciprocal space maps are shown for (c) LSCO/STO and (d) LSCO/LAO thin films and demonstrate the in-plane lattice matching and out-of plane relaxation of LSCO. The substrate as well as thin film peaks are broader for LSCO/LAO.

Based on the data reported in the ref. 20 we estimate the coefficient of the oxygen nonstoichiometry δ . In agreement with the TEM data δ for LSCO/LAO is significantly lower 0.04 than for LSCO grown on the STO substrate 0.14.

Q7: page 8, the determination of the diffusion coefficient is not hampered by these surface effects, Sr segregation. However, the strained films used in this study may have the surface Sr segregation depending on the strain state and/or the quality of the films. This will influence the oxygen surface exchange kinetics. Did the authors confirm no Sr segregation or no discernible surface difference in the films used?

R: We did not observe any Sr segregations at the interface with the substrate. The corresponding EDX elemental maps of whole cross-sections of the LSCO films are included to the Supplementary Information.



Q8: page 10, The authors mentioned that it was not possible to find a suitable temperature for exact determining D^* of both strain states for the reasons described there 9. The authors are suggested to state more details of the reasons described in the reference.

R: We added the following discussion in the text of revised manuscript: “For LSCO64 it was not possible to find suitable conditions for exactly determining the high D^* of the tensile strain state.[Ref. 9] Reason is that incorporation is surface limited and our investigated diffusion length is small due to the 20 nm thin films. Therefore, when performing the experiment at the low temperatures/times necessary for achieving a diffusion length in the order of the film thickness, virtually no ^{18}O is incorporated via the surface. For higher temperatures/times where detectable amounts ^{18}O are incorporated, a lower boundary for D^* could be determined, see the arrows in Fig. 5.”

Q9: page 12, Fig 6. What is the direction of the vacancy ordering in LSCO/LAO? As the authors pointed out, it is believed that oxygen vacancies can increase the unit cell volume of LSCO. In Fig 6e, the authors estimated the volume of the bulk LSCO assuming a simple elastic model. If this estimation is correct, this data represents more oxygen vacancies in the bulk LSCO compared to the compressive strained LSCO film. How is the volume of the bulk LSCO without any modulation? Is it still larger than that of LSCO/LAO films?

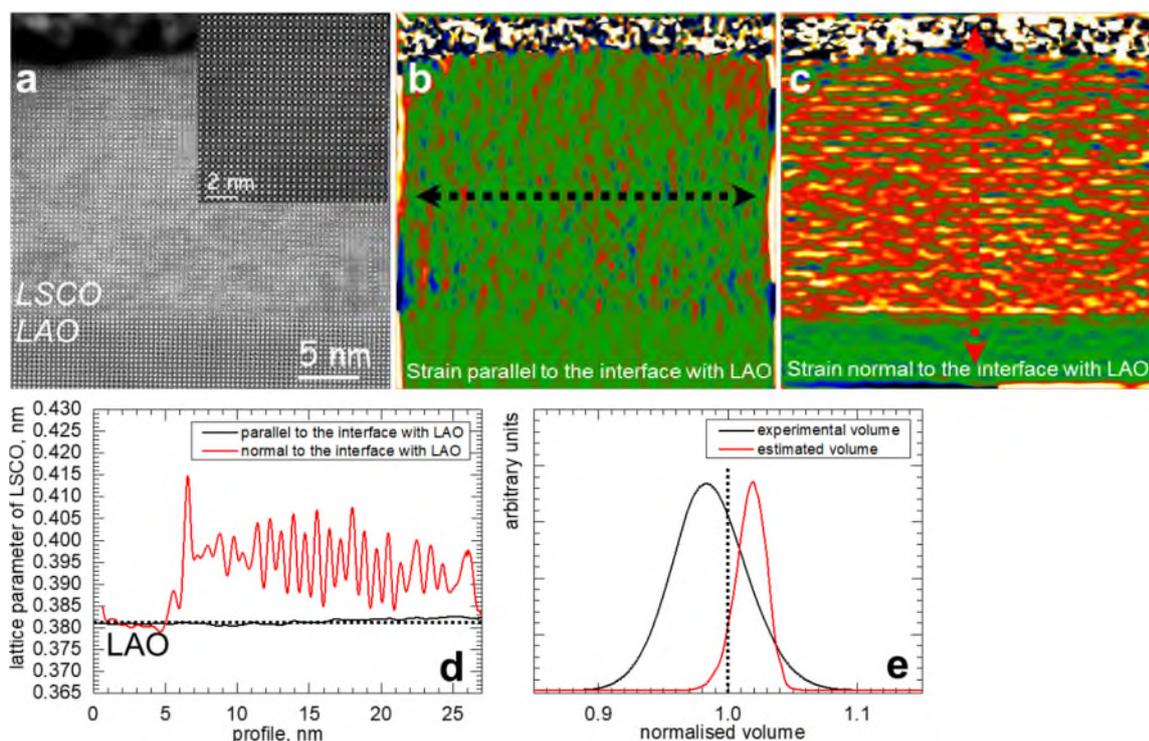
R: As we mentioned before, for LSCO grown on LAO substrate there is a local modulation of the out-of plane lattice parameter with 2 unit cells periodicity similar to the Brownmillerite phase. We assume this is due to the oxygen vacancies ordering. For the reported Brownmillerite phase of LSCO the lattice parameter oscillates between 3.783 and 4.527 Å [30], the last one corresponds to the oxygen-depleted atomic rows. In our case the lattice parameter oscillates between 0.38 and 0.41 Å, the last value is significantly lower in comparison with the oxygen-depleted atomic rows in the Brownmillerite phase of LSCO but a bit larger than it is expected from the simple Poisson model. Thus, we conclude there is an oxygen vacancy ordering in LSCO64/LAO, but it is significantly lower than for LSCO64/STO.

Figure 6 shows the volumes normalized on the volume of the bulk LSCO, so 1.0 corresponds to the bulk value. By using a simple elastic model, we try to separate compressive strain induced by LAO substrate and the lattice expansion due to the oxygen non-stoichiometry. But obviously, the whole picture is more complicated. It is clear, the average measured atomic volume is lower than it should be if taking into account only the strain induced by the substrate. The volume distribution is very wide as well, reflecting non homogeneous out-of plane strain map shown on the figure 6c. There are regions with the atomic volume been larger than the estimated values and the bulk value. What is why we focus on the local atomic structure rather than on the comparison with the bulk properties which is not so straightforward.

Q10: page 13, In Fig 7e, the volume of the LSCO/STO film is similar to that of the expanded bulk LSCO. Does this data represent both the LSCO/STO film and the bulk LSCO have a similar level of oxygen vacancies? In Fig 7a, the authors showed the magnified HAADF image showing the formation of BM phase. It is good to add the magnified HAADF image showing the BM phase in the LSCO/LAO in Fig 6.

R: Similar to the previous comment, it is not so simple to evaluate the difference on the level of oxygen vacancies between the bulk material and the strained epitaxial thin film. We used bulk volume of LSCO only for normalization of the measured and estimated (from the simple elastic model) volume of epitaxial film. It is clear from the Figure 7e LSCO grown on STO has an average atomic volume equal to the reported bulk value, but the expected value due to the tensile strain induced by the substrate should be smaller. Thus, it is definitely attributed to the effect of the oxygen vacancies ordering, which is much more pronounced than in the case of LAO substrate. The amount of the measured volume larger than the bulk value is significantly higher for LSCO grown on STO. It is related to the regions with the BM phase. In that case the local oscillation of the lattice parameter is close to the reported Brownmillerite phase of LSCO.

We added the magnified STEM image on the Figure 6.



Q11: page 16, In Fig. 8, the authors compared EELS data of the LSCO/STO and LSCO/LAO. The authors argued that there is no pronounced difference between O-K edges collected from the different Co atomic rows for LSCO deposited on the LAO substrate in contrast to the LSCO/STO. However, the data show no pronounced difference between O-K edges collected from the different Co atomic rows for both LSCO/STO and LSCO/LAO as compared to the data in Ref. 28 and another reference (see PRL 112, 087202, 2014). The authors should rewrite their argument. If necessary, the authors are suggested to include more clear data about O-K edges.

R: Indeed, the difference between O-K edges collected from the different Co atomic rows for LSCO deposited on the STO substrate is not so pronounced as it was reported in the Ref. 28 and (PRL 112, 087202, 2014). The reason is the overall spatial resolution, in our case the probe size is about 1.4 Å. Nevertheless, the main feature is the same, the integrated intensity for the dark stripe is smaller in comparison with the adjacent bright stripes. In contrary, the difference between O-K edges collected from the different Co atomic rows for LSCO deposited on the LAO is within the noise level.

But since those results do not show sufficiently new data, we moved it to the Supplementary Information.

Q12: page 17. The authors calculated the oxygen non-stoichiometry of the LSCO films based on their GPA data. However, GPA data only represents the localized area of the LSCO films. It cannot represent the overall feature of the LSCO films. The authors obtained 0.05 for the LSCO/LAO and 0.22 for the LSCO/STO films. Considering the typical δ values of the bulk LSCO (0.01 – 0.02), the reviewer cannot trust the obtained δ values for the LSCO films. If the obtained δ values for the LSCO films are correct, how can the authors explain the volume comparison in Fig. 6 and 7 based on the obtained δ values?

R: We attempted to perform those estimations based on the average lattice parameter calculated across the LSCO film cross-sections and approach reported in Ref. [30]. But in fact, it is smaller than the difference observed in our tracer diffusion coefficients (a factor of 300!). It means that not just oxygen vacancy concentration but rather the local atomic structure plays a major role in the oxygen exchange kinetics. The oxygen vacancy ordering in tensile strained LSCO releases the strain induced by the substrate and creates locally oxygen depleted atomic rows similar to BM phase. In contrary, the compressive strained LSCO film stays strained relatively to both the LAO substrate and its bulk value. There are only some regions with the lattice parameter to be slightly larger than the value estimated from the simple elastic model. Moreover, the average volume is smaller than expected related to the effect of the oxygen vacancies ordering (BM phase like modulations of the lattice parameter in the growth direction).

Moreover, we attempted to estimated δ values from new XRD data based on the approach reported in²⁰ and the results are similar to ones obtained from TEM study (see the discussion above).

Q13: In general, the k^* and δ value of the bulk LSCO (Sr=0.4) are $\sim 4 \times 10^{-8}$ and 0.02, respectively ($\sim 550 - 650$ O C, 1atm). In this manuscript, the authors obtained the k^* of $\sim 1 \times 10^{-8}$ for the tensile strained LSCO that has δ of 0.22 and the k^* of $\sim 1 \times 10^{-10}$ for the tensile strained LSCO that has δ of 0.05. Then, δ seems to have no effect on the oxygen surface exchange kinetics for LSCO. The authors should provide clear and detailed explanations of it.

R: We added the following text to the revised version: “The observed difference in k^* for the two strain states was about 1-2 orders of magnitude in the investigated temperature interval. As discussed above, k^* values were in general smaller than literature which we attribute to adverse effects from ion irradiation. Consequently, the differences may also be influenced by different relaxation of the free-cut surfaces or similar and the focus is laid on the diffusion characteristics.”

Q14: Overall, the authors argument that the role of oxygen vacancy ordering in transport and surface exchange kinetics for LSCO is not clear. For example, the authors only emphasized that all the properties of LSCO/STO (tensile strained film) are related to a BM like superstructure. It is known that the oxygen vacancy ordering in LSCO eventually forms a BM-like superstructure. What is the role of BM like superstructure in transport and surface exchange kinetics for the compressive strained LSCO films? In addition, the authors did not provide any theoretical prediction of the formation energy of oxygen vacancies. But, the authors claimed that in their conclusion. Where is it from?

R: BM phase is known to form in epitaxial LSCO films to release the strain induced by the substrate. And it is typically observed at higher Sr concentration than 40%. Our LSCO/STO films fully accommodates the strain from the substrate by forming locally BM like superstructure at lower than expected Sr doping level. It assumes larger value of the oxygen vacancies concentration than in the bulk material.

Similar but significantly weaker effect of the oxygen vacancy ordering has been found in the LSCO/LAO epitaxial film. There is weak 2 unit cells periodicity of the lattice parameter in the growth direction. But the concentration of the oxygen vacancies is not enough to release the strain induced by the mismatch with the LAO substrate.

We agree with referee, we did not perform any theoretical calculations on the formation energy of oxygen vacancies. The sentence in the conclusion: “Additionally, it is theoretically predicted that the oxygen vacancy formation energy decreases significantly with an increase in the Co spin state.” - is related to the literature, ref. [28] as discussed in the text. In the revised version we clarified this statement: “As reason behind these differences we assume a significantly changed oxygen vacancy formation enthalpy with mechanic strain and the Co spin state in accordance with literature”

Reviewer 2:

In this paper the authors have prepared thin films of LSC perovskite deposited on STO or LAO substrates in an effort to induce either compressive or tensile strain. They then use microscopy and isotopic exchange to study the oxygen transport characteristics of these films and correlate differences in the transport with structural changes, suggesting that a brownmillerite phase is formed in one case.

Q1: Much of the case is made through interpretation of the TEM data using the GPA methods, with modulation ascribed to oxygen ordering. As the interpretation of subtle features in the GPA data are central to this paper it is disappointing that further details of the method employed are not included. I also find it surprising that some details of the film quality, thickness etc are not provided. What thickness film is deposited? Is the strain state maintained throughout the film, or only close to the interface with the substrate? Assuming that there is a strain gradient away from the interface, would this affect the interpretation of the diffusion data?

R: The detailed description of the GPA method used for analysis is given in the ref. 19. The corresponding script for Digital Micrograph is available on-line, ref. 20.

In the Material and Methods section of our original manuscript, we stated the film thickness: “Epitaxial $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ thin films with ~20 nm thickness were prepared on $10 \times 10 \times 0.5 \text{ mm}^3$ LaAlO_3 and SrTiO_3 (100) single crystals (Crystec, Germany) by pulsed laser deposition”. The TEM-lamella thicknesses were in good agreement with the expected thicknesses from PLD deposition, for which growth rates are determined using stylus profilometry.

The Figure 6 and 7 show the full map of the strain components in-plane and out of plane to the substrate across the LSCO film thickness as well as the corresponding profiles. For LSCO/LAO film the in-plane component is almost constant from interface with the substrate towards film surface, the out-of-plane component shows the slight relaxation to the bulk value of LSCO. For LSCO/STO film there is no pronounced difference in the average lattice parameter across the thickness of the film.

The corresponding discussion is added to the text: “The strained state of the LSCO film grown on the STO substrate is maintained through its thickness (20 nm). For LSCO/LAO film the map on the figure 6c indicates only slight relaxation of the out-of-plane lattice parameter to the bulk value of LSCO towards the film surface.”

Q3: Additionally the preparation of the trench in the film using the FIB has been known to induce amorphisation of the film edges. Have the authors verified that there is no damage induced by the FIB milling, and that this does not have an effect on the surface exchange coefficients measured?

R: Indeed, ion beam damage / amorphisation on film etches is generally hampering very active surfaces. Here, we strongly suspect that this is the reason for the lower k^* compared to literature which we discuss on p8 of the manuscript “Additionally, the free LSCO surface was created by ion beam etching. The high energy ions can certainly damage the surface upon impact, which explains both a lower surface exchange compared to literature²² and a large scatter. Additionally, in the investigated temperature range, also Sr segregation²³ at the surface may reduce the surface exchange. However, the determination of the diffusion coefficient is not hampered by these surface effects as the profiles propagate over several μm , much deeper than the few nanometers deep zone where LSCO may be altered by ion beam damage or Sr segregation.”

This also is the reason why we laid focus on the interpretation of the D^* over the k^* values. Despite being most probably affected from the ion beam etching, we found it important to report the values and according differences in k^* .

To make these points clearer for the reader, we added in the text: “The observed difference in k^* for the two strain stated was about 1-2 orders of magnitude in the investigated temperature interval. As discussed above, k^* values were in general smaller than literature which we attribute to adverse effects from ion irradiation. Consequently, the differences may also be influenced by different relaxation of the free-cut surfaces or similar and the focus is laid on the diffusion characteristics.”

Q4: There are also questions regarding the exchange experiments. The oxygen 16 anneal and the oxygen 18 anneal are both of 1 hour duration. Normally an oxygen 16 anneal is undertaken for significantly longer than the exchange anneal to ensure that the material is equilibrated, and has little to do with the background oxygen 18 concentration, other than to ensure absolutely that all measured oxygen 18 is from the exchange anneal. This is critical to ensure that a self diffusion experiment is performed and that there is no chemical diffusion. Can the authors confirm that they have verified that their exchange conditions have not induced any chemical diffusion?

R: Clearly the reviewer is correct, and for a typical diffusion experiment we would have chosen a factor 4-10 higher pre-annealing time. For this in-plane diffusion experiment, we had to find a trade-off between lateral resolution in ToF-SIMS and Sr-segregation/interface reactions. In order to investigate the in-plane profiles, they need to be several μm long, which requires temperatures way $>600^\circ\text{C}$ (680°C and higher in this work). There, however, it is known that Sr segregation, and from $\sim 750\text{-}800^\circ\text{C}$ also interface reactions with the substrates can occur in few hours. That is why we needed to keep the total time at elevated temperature as short as possible. As LSC is a fast electronic conductor, so chemical diffusion is significantly faster than tracer diffusion (typical ~ 2 orders of magnitude, depending on the vacancy concentration). Consequently, we chose a 1h pre-annealing step in order to reduce irreversible changes of the sample.

We exclude chemical driven tracer incorporation to affect our results as (i) no deviations from regular profile shape was observed (chemically driven incorporation creates sharper profiles) and (ii) Small pinholes were present in all samples' capping layer, which manifested in a slightly elevated 18O background (~ 0.028 instead of 0.0205 in our 18O experiment. For chemical equilibration of the sample these act as fast equilibration channels thus significantly reducing the otherwise long in-plane diffusion path necessary (5mm) to the μm range.

Q5: Also, the surface exchange data plotted in Figure 4 suggest a difference of 30-60 times between strain states. Does this range include the maximum extent of the experimental uncertainties plotted?

R: Thanks to the referee, we did not properly include the uncertainty here. We changed this to: “The observed difference in k^* for the two strain states was about 1-2 orders of magnitude in the investigated temperature interval.”

Q6: It would also be useful to compare how these strained data compare with bulk materials - is there any variation away from bulk properties. If there is that would surely strengthen the argument regarding the structural influence.

R: We used bulk volume of LSCO for normalization of the measured and estimated (from the simple elastic model) volume of epitaxial films on the Figure 6 and 7. In contrast with the bulk material a brownmillerite phase (BM) is known to form in epitaxial LSCO films to release the strain induced by the substrate. And it is typically observed at higher Sr concentration than 40%. Our LSCO/STO films fully accommodates the strain from the substrate by forming locally BM like superstructure at lower Sr doping level. It assumes larger value of the oxygen vacancies concentration than in the bulk material.

Similar but significantly weaker effect of the oxygen vacancy ordering has been found in the LSCO/LAO epitaxial film. There is a weak 2 unit cells periodicity of the lattice parameter in the growth direction. But the concentration of the oxygen vacancies is not enough to release the strain induced by the mismatch with the LAO substrate.

Comment: Overall this is an interesting paper with useful new data, but there are some significant areas where there could be improvements made.

R: We would like to thank Reviewer 2 for finding our work interesting. We considered carefully all the technical points raised by the referee.

Reviewer 3

Comments: The authors report an study of oxygen diffusion in LSCO ($x=0.4$) thin films under different degrees of epitaxial strain. The surface exchange coefficient, k^* , and diffusion coefficient, D^* , were determined by ^{18}O -isotope exchange ToF-SIMS experiments. The authors found important differences in oxygen diffusion between both types of films, with both diffusion and exchange increasing substantially with tensile strain. A microstructural study reveals that the concentration of O-vacancies is larger in the tensile-strained thin film, which transforms into a brownmillerite (BM) phase. My main criticism to the paper is about its novelty. Some of the authors published a paper in ACS Nano 3276 (2013) with a very similar study on similar samples (over similar substrates) in which both k^* and D^* were studied by ToF-SIMS to conclude that “much faster surface exchange (4 times) and diffusion (10 times) were observed for the tensile strained films compared to the compressively strained films in the entire temperature range”. This is basically the same conclusion as here.

From this point of view, only the link between the increase of k^* and D^* with tensile strain and the formation of the BM phase could be considered as an original contribution. However, the

formation of the BM is also well known in these oxides and the effect of strain well documented (ref. 28, 29, and many more in the recent literature).

Comment: In summary, I do not think this paper adds anything useful to the literature of oxygen diffusion in Co oxides, and therefore I cannot recommend its publication.

R: We hope to have presented our case more convincingly in this revised version and want to highlight the following novelties our publication adds to literature.

The current submission sheds light on the local atomic structure of the epitaxial LSCO films grown on the STO and LAO substrates with opposite sign of the strain induced. In fact, the tensile strain induced by the STO substrate is fully accommodated by the mechanism typically observed in the film with higher Sr doping – the formation of BM-like superstructure. There are domains with orthogonal orientations of the oxygen depleted atomic rows. In contrary the LSCO film grown on the LAO substrate stays strained relatively to the substrate although a slight modulation of the out-of plane lattice parameter similar to the BM-like superstructure is found.

We also present new measurements to complete the study of the substrate induced strain effect on the oxygen exchange kinetics in the both in-plane and out of plane geometry. As a result, we can clearly confirm for both parameters the diffusion coefficient D^* and the surface exchange parameter k^* that the tensile strain leads to faster diffusion and oxygen exchange independently on the experiment geometry. Taking into account the fact that polycrystalline film shows similar data to the tensile strained LSCO, one can conclude based on our structural data, the strained state of LSCO epitaxial film on LAO is not good for oxygen exchange kinetics. We also emphasise the role of BM like superstructure in the enhanced properties of LSCO grown on STO. The structural data also explain the absence of the pronounced difference for the results obtained in-plane and out of plane geometry.

Q1: On the other hand, the discussion of some parts (results) is very poor. For instance, the differences between D^* and k^* with literature values are only mentioned but deserve a much deeper discussion. Also, the discussion of the EELS data is rather limited and the justification of the high/low spin state of Co is completely speculative, without any evidence from their data to support it. Sentences like “the high spin state of Co₂rows in the browmillerite phase could additionally contribute to the observed difference in the oxide ion diffusion kinetics”, need, at least, and explanation. How do the authors think this could happen? Are they proposing a change in the hybridization of Co-O bond so the formation/mobility of O-vacancies changes with the spin state, or it is only related to a volume effect? How would this impact anisotropic O-diffusion/exchange?

R: We modified the Figure 5 for better comparison with the data in literature as well as added the related discussion in the revised version of the manuscript: “Comparison of thin film samples to bulk LSCO (iv) shows that even for the tensile strain state, the high bulk diffusion coefficients are not fully reached, despite higher vacancy concentrations are present in tensile thin films. Consequently, the mobility of vacancies has to be reduced in tensile thin films, which is not surprising as strong defect interactions and vacancy ordering as observed. Similar observations of higher vacancy concentration but lower mobility were reported in literature e.g. in vicinity of dislocations for SrTiO₃,^{23,35} or for acceptor doped ceria.³⁶”

The sentences “the high spin state of Co₂ rows in the brownmillerite phase could additionally contribute to the observed difference in the oxide ion diffusion kinetics” is related to the part of the discussion on the page 17: “This is in agreement with the previous study [28]. The fine structure of the OK edges from dark stripes on HAADF image (Co₂ rows) reflects the decrease of oxygen content, although the analysis of the fine structure of the Co-L23 edge does not show the change of the Co valence state. First-principles calculations provided an interpretation based on a model of nanometer sized pockets with high-spin Co ions in the Co₂ planes containing O vacancies, and low-spin Co ions in the Co₁ planes [28]”. To make it clear, we now include the reference [28] to the conclusion as well.

Decision letter and referee reports: second round

26th Mar 20

Dear Dr Ivanov,

Your manuscript titled "Strain induced structure and oxygen transport interactions investigated on epitaxial La_{0.6}Sr_{0.4}CoO_{3-δ} thin films" has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

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* Please consider the following revised title and abstract, which have been edited to meet our house style and for clarity. Please note that I have suggested an additional sentence at the end of the abstract regarding how this research might be useful; please edit this as you see fit.

Title: Strain-induced structure and oxygen transport interactions in epitaxial La_{0.6}Sr_{0.4}CoO_{3-δ} thin films

Abstract: The possibility to control oxygen transport in one of the most promising solid oxide fuel cell cathode materials, La_{0.6}Sr_{0.4}CoO_{3-δ}, by controlling lattice strain raises questions regarding the contribution of atomic scale effects. Here, high-resolution transmission electron microscopy revealed the different atomic structures in La_{0.6}Sr_{0.4}CoO_{3-δ} thin films grown under tensile and compressive strain conditions. The atomic structure of the tensile-strained film indicated significant local concentration of the oxygen vacancies, with the average value of the oxygen non-stoichiometry being much larger than for the compressive-strained film. In addition to the vacancy concentration differences that are measured by isotope exchange depth profiling, significant vacancy ordering was found in tensile-strained films. This understanding might be useful for tuning the atomic structure of La_{0.6}Sr_{0.4}CoO_{3-δ} thin films to optimize cathode performance.

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"Strain engineering can enhance oxygen transport in cathodes in solid oxide fuel cells. Here, atomic scale imaging is used to probe local structures in tensile- and compressive-strained La_{0.6}Sr_{0.4}CoO_{3-δ} films, revealing higher oxygen vacancy concentration in tensile films, and vacancy ordering."

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REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The authors have responded to my previous comments appropriately and revised the manuscript accordingly. I recommend the acceptance of the revised manuscript.

Reviewer #2 (Remarks to the Author):

The authors have addressed the comments of this reviewer to a satisfactory extent and I am happy to recommend that it is now published. Only one minor issue - the new RSM data are labelled as Fig X and should clearly be Fig 6, and all other figs need to be renumbered.

Reviewer #3 (Remarks to the Author):

Dear Editor

Thank you for sending me the revised version of this paper. I think the authors improved the manuscript after incorporation of the suggestions of the referees. Although I am not sure my main criticism, related to the publication by some of the authors of a paper in ACS Nano 3276 (2013) with a very similar study on similar samples, is completely refuted by the authors, I guess the incorporation of new data/discussion adds some novelty to the data. Therefore, I have no strong arguments about publication of the present version.

Author rebuttal letter: second round

Dear Editor,

We would like to thank the referees for finding our work interesting and worth to be published in Communications Materials

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R: We have corrected the numbers of the figures in the final version of the manuscript.

Reviewer #3 (Remarks to the Author):

Dear Editor, Thank you for sending me the revised version of this paper. I think the authors improved the manuscript after incorporation of the suggestions of the referees. Although I am not sure my main criticism, related to the publication by some of the authors of a paper in ACS Nano 3276 (2013) with a very similar study on similar samples, is completely refuted by the authors, I guess the incorporation of new data/discussion adds some novelty to the data. Therefore, I have no strong arguments about publication of the present version.