Web links to the author's journal account have been redacted from the decision letters as indicated to maintain confidentiality.

Decision letter and referee reports: first round

28th Apr 20

Dear Prof Íñiguez,

Thank you for submitting your manuscript, "Antiferroelectricity in a family of pyroxene-like oxides with rich polymorphism", 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 considerable interest, they have raised substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication in its present form, but would be interested in considering a revised version that addresses these important points.

We hope you will find the referees' comments useful as you decide how to proceed. In particular, you will see that Reviewer #2 is concerned about the lack of a quantitative discussion on the proposed solid-solutions as potential routes towards realistic antiferroelectric candidates. Furthermore, Reviewer #3 is requesting important technical details regarding your MD and NEB calculations such as length of trajectories, time steps, and (meta)stability of the solutions at various temperatures. We would naturally expect the other requests and comments of the referees to be appropriately responded to, including their requests for further information and discussion.

We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns before we make a final decision on publication. Should further discussion and analysis allow you to address these criticisms, we would be happy to look at a suitably revised manuscript. 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 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. Clicking this link will download a zip file containing the pdf.

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 **

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

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,

Dr Aldo Isidori
Associate Editor
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This is an interesting study of the computational discovery of a new family of antiferroelectrics, based on vanadates like KVO3.
Using state of the art tools such as MD, structural minimization,
harmonic phonon calculations, etc. the authors convincingly demonstrate the instability of the perovskite structure to two
bond ruptures leading to a structure with networks of tetrahedrally coordinated V which carry dipoles arranged in an antiferroelectric pattern. They furthermore find a path to a corresponding ferroelectric phase and estimate the size of
the electric field required to overcome the barriers between the two phases. While these fields are large, the authors correctly point out that estimating the coervice fields even in ferroelectrics are usually overestimated by such calculations on idealized crystals not taking into account the real materials
imperfections that are known to affect such transitions and effects such as domain boundary pinning, nucleation and growth of domains etc. I agree with the authors that these are beyond the scope of a first-principles investigation. They also provide guidance on how the materials could be further improved by chemical tuning. So, this is an excellent paper and I recommend publication essentially without change.
I just have a few small optional suggestions:
1) When showing the bond ruptures, what is the criterion on
interatomic V-O distance used to conclude there is a a bond or
not?
2) When comparing the spontaneous polarizations to those of
BaTiO3, they say they are of the same order of magnitude but
they seem to be a factor 5 to 10 smaller. That is still sizable but I wouldn't call it the same order of magnitude if they differ
by almost a factor 10.
3) when discussing antipolar vs. polar unstable modes in the supplemental information, I assume by polar they mean the mode
at Gamma having imaginary frequency and by antipolar they mean the modes at the Brillouin zone boundaries. It might be worth
mentioning this explicitly. These modes appear to be unstable

over the whole Brillouin zone. Can they comment on the implication of this?

Reviewer #2 (Remarks to the Author):

Several members of a family of ABO3 pyroxene-like compounds are proposed as candidate antiferroelectrics based on first principles calculations. First, a materials discovery strategy is proposed that consists of comparing the energy of polar and antipolar structural distortions from a high-symmetry reference state, which in the present manuscript is taken to be the cubic perovskite structure. Second, three materials are identified in which the antipolar state is slightly lower in energy than the polar state, suggesting that it may be possible to convert between the two with an applied electric field, thus leading to antiferroelectric behavior. Third, reaction paths connecting the polar and antipolar states are identified, and it is found that applying an electric field may lower the transition barriers between the different structures, but not at realistically experimental fields.

Materials discovery is a challenging problem, but high-throughput searches have recently shown promise to tackle it. The present study proposes a strategy to use high-throughput calculations to discover candidate antiferroelectric materials. This is an interesting idea, but the authors should consider the following comments to clarify their strategy:

1. The starting point of the study is a high-throughput framework to identify potential antiferroelectric materials by studying the symmetry-lowering distortions of a reference cubic perovskite structure. However, barely any details are given about this process, which will make it difficult for readers to gauge its potential. For example, how many compounds were tried and what was the success rate? How were these initial compounds chosen? And why? These are essential questions so that others can take this approach forward.

2. Why is molecular dynamics a good way of determining the ground state? Could a MD simulation not lead to the system being stuck in a local minimum and never reach the global minimum? Why did the authors not use standard structure prediction methods to explore configuration space more uniformly? Or perhaps enumerating symmetry-broken distortions? In this particular instance the predicted structure agrees with experiment, but is this approach generalizable when experiment is not available?

3. The studied vanadates turn out to be poor antiferroelectric candidates because the electric fields needed are too large. In the discussion, the authors qualitatively discuss a number of potential routes to perhaps make these or similar compounds work. Why did the authors not test these guesses?

And some minor comments:

4. Typo: Fig. 3g should read Fig. 2g in the text.

5. The introduction mentions four vanadates, but NaVO3 is not mentioned again. Why is that?

Reviewer #3 (Remarks to the Author):

The manuscript proposes a computational strategy to discover new possible antiferroelectric (AFE) material candidates, based on multiple density functional theory (DFT) methods including phonon calculations, ab-initio molecular dynamics (DF-MD) simulations, and nudged elastic band (NEB) calculations. The approach is applied to the alkali vanadates, where possible antiferroelectricity is

demonstrated. The universality of the approach is further discussed with respect to compositions and for other compounds.

Overall, the results are novel, the study is technically thorough, and the manuscript reads well. Since the study could potentially motivate future computational and theoretical research towards exploring new AFE materials, it is of high interest to the ferroics research community. Thus, I think the manuscript fits the Communications Materials publication requirements well. I do, however, have some comments and concerns (remark 1-7) that must be addressed by the authors before I can recommend the manuscript for publication. I also have some minor comments and suggestions (remark 8-13) that might strengthen the manuscript and/or motivate further work. Please find my comments below.

1.
On page 1 in the manuscript, it is stated that "alkali vanadates ($NaVO_3$, KVO_3, $RbVO_3$ and $CsVO_3$) show dominant and related polar and antipolar soft modes". While results for KVO_3, $RbVO_3$ and $CsVO_3$ are all reported, there are no results shown for $NaVO_3$. Either additional results for $NaVO_3$ must be added to the manuscript and/or the supplementary information, or it must be clearly justified why the results for $NaVO_3$ are omitted.

2.
On page 1 in the manuscript, it is stated that "first-principles molecular dynamics simulations ... reveal the existence of numerous low-energy metastable polymorphs". Are these polymorphs observed to be (meta)stable for all of the temperatures investigated (10 K to 1000 K), or only some of them? Do elevated temperatures induce any structural phase transitions between the polymorphs that might complicate the finite temperature AFE behavior discussed (e.g. in Fig 3)?

3.
Also in regard to the DF-MD simulations:
In what order of magnitude are the trajectory lengths for the DF-MD calculations, and what time steps are used? In order to validate the claimed structural (meta)stabilities from the DF-MD calculations, typical trajectory lengths and the time steps in the DF-MD simulations must be included in the manuscript.

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On page 2 in the manuscript it is stated that "The ZZ structure is the most stable one, the lowest-energy BM and RG structures lying 117 meV and 125 meV per formula unit (f.u.)". It is not clear if these values are equal for all of the vanadates investigated or if they are from one specific model system and must be commented accordingly.

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The NEB path in Fig. 3(a) is extended up to "a FE state in which the polarization lies fully out-of-plane". As becomes apparent from the calculated MEP, and also addressed in the manuscript, this structure lies on a saddle point along the MEP. Is this FE structure structurally relaxed prior to the NEB calculation? I suspect that this structure is unstable and will relax back to the ZZ-F structure (or some other (meta)stable structure), unless this FE configuration itself is (highly) metastable?

6.
How did the authors calculate the polarization along the hysteresis-loops in Fig. 3(b) and Suppl. Fig. S2(b)-(e)? Is it extrapolated from the zero-field results assuming a linear dielectric response, and if so, which values of the dielectric constants (or dielectric susceptibilities) were used? This is unclear and must be explained in more detail.

7.
Regarding the methods section, the following essential details are missing and must be included or specified in the manuscript:

- Which electrons where treated as valence electrons - or - Which specific PAW potentials supplied with VASP were used?
- What convergence criterion is used for the NEB calculations? Did the authors use the same criterion as for the structural relaxations (i.e. 0.01 eV/A)?
- How long trajectories were typically calculated in the DF-MD simulations? (See also comment #3 above).
- What time step is used in the DF-MD calculations? (See also comment #3 above).

8.
Is it possible to add a pseudo-cubic coordinate axis to Fig. 1 and to Suppl. Video #2, similar to those in Fig. 2? This will aid the reader to connect the structures in all the figures and videos to that of the perovskite structure in Fig. 1 (a). I would like to express my appreciation for the supplementary videos included, since they are very useful aids for the reader to clarify the phase transitions investigated.

9.
In Fig. 2 (e)-(f) it is difficult to distinguish the difference in the out-of-plane polarization component between the different structures, since the out-of-plane polarization is parallel to the view direction. Could the authors specify what the green and red arrows correspond to in the figure caption? Since the out-of-plane polarization is of the main interest in this study, it would be helpful to the reader to also include an illustration where the out-of-plane polarization component is perpendicular to the view direction to more clearly visualize the relative differences.

11.
Adding calculated electronic density of states (DOS) for the ZZ-A and ZZ-F polymorphs could be useful. While this is not the focus of the study, it will give proof that the materials investigated are electronically insulating, a prerequisite for (anti)ferroelectricity. Even though this is inferred by the calculated spontaneous polarizations, electronic DOSes will explicitly confirm this.

12.
It is a justified choice that the manuscript focuses mainly on the results of the ground state ZZ polymorph in KVO3, as a proof-of-concept for the proposed AFE screening approach. While the following is beyond the scope of the manuscript, if the authors want to further extend the study, I would suggest to also include results for the AFE switching of the two other vanadate model systems investigated, similar to that reported for KVO3 in Fig. 3 and Suppl. Fig. S2. This will add additional proof that the approach works for all the compounds investigated, and could strengthen the overall story.

13.
List of typos:
- On page 2 in the manuscript it is stated that "... the ZZ-F polymorph is shown schematically in Fig. 3g". The ZZ-F polymorph is shown in Fig. 2(g).
- On page 2 in the manuscript it is stated that "... an intermediate ferrielectric state (ZZ-i), with half of the tetrahedra in one of the chains flipped (Fig. 3f) ...". The ZZ-i polymorph is shown in Fig. 2(f).

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This is an interesting study of the computational discovery of a new family of antiferroelectrics, based on vanadates like KVO_3. Using state of the art tools such as MD, structural minimization, harmonic phonon calculations, etc. the authors convincingly demonstrate the instability of the perovskite structure to two bond ruptures leading to a structure with networks of tetrahedrally coordinated V which carry dipoles arranged in an antiferroelectric pattern. They furthermore find a path to a corresponding ferroelectric phase and estimate the size of the electric field required to overcome the barriers between the two phases. While these fields are large, the authors correctly point out that estimating the coervice fields even in ferroelectrics are usually overestimated by such calculations on idealized crystals not taking into account the real materials imperfections that are known to affect such transitions and effects such as domain boundary pinning, nucleation and growth of domains etc. I agree with the authors that these are beyond the scope of a first-principles investigation. They also provide guidance on how the materials could be further improved by chemical tuning. So, this is an excellent paper and I recommend publication essentially without change. I just have a few small optional suggestions:

1) When showing the bond ruptures, what is the criterion on interatomic V-O distance used to conclude there is a bond or not?

Bonds between the V and O atoms are drawn if the V-O distance is at most 25% larger than in the cubic perovskite phase. For KVO_3 the maximum V-O distance for which we draw V-O bonds is 2.5 Angstrom. We now state this explicitly in the Methods section.

2) When comparing the spontaneous polarizations to those of BaTiO3, they say they are of the same order of magnitude but they seem to be a factor 5 to 10 smaller. That is still sizable but I wouldn't call it the same order of magnitude if they differ by almost a factor 10.

We have changed the statement to reflect the fact that the obtained polarisation for KVO_3 is 5 times smaller than of $BaTiO_3$.

3) when discussing antipolar vs. polar unstable modes in the supplemental information, I assume by polar they mean the mode at Gamma having imaginary frequency and by antipolar they mean the modes at the Brillouin zone boundaries. It might be worth mentioning this explicitly. These modes appear to be unstable over the whole Brillouin zone. Can they comment on the implication of this?

The referee is correct, we were referring to the modes with imaginary frequency at Gamma (polar) and at the zone boundaries (antipolar). We now explicitly mention it in Supplementary Note 1 as suggested by the referee.

Then, as the referee mentions, we do obtain a very flat band across the Brillouin zone and connecting the polar instability in Gamma with the antipolar ones at zone-boundary points. This is typical of ideal (Kittel-like) antiferroelectric materials, as for example discussed in a recent publication by Milesi-Brault et al. (Phys. Rev. Lett. 124, 097603 (2020)), and could have implications for the character of the phase transition (which can be expected to be of the order-disorder type). We have inserted a brief comment on this point in the revised Supplementary Note 1.

Reviewer #2 (Remarks to the Author):

Several members of a family of ABO_3 pyroxene-like compounds are proposed as candidate antiferroelectrics based on first principles calculations. First, a materials discovery strategy is proposed that consists of comparing the energy of polar and antipolar structural distortions from a high-symmetry reference state, which in the present manuscript is taken to be the cubic perovskite structure. Second, three materials are identified in which the antipolar state is slightly lower in energy than the polar state, suggesting that it may be possible to convert between the two with an applied electric field, thus leading to antiferroelectric behavior. Third, reaction paths connecting the polar and antipolar states are identified, and it is found that applying an electric field may lower the transition barriers between the different structures, but not at realistically experimental fields.

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1) The starting point of the study is a high-throughput framework to identify potential antiferroelectric materials by studying the symmetry-lowering distortions of a reference cubic perovskite structure. However, barely any details are given about this process, which will make it difficult for readers to gauge its potential. For example, how many compounds were tried and what was the success rate? How were these initial compounds chosen? And why? These are essential questions so that others can take this approach forward.

We thank the referee for pointing this out. While this article is focused on the predicted antiferroelectric behaviour of a particular set of materials, it is true that it can be useful to provide some additional information on the calculations that led to identifying the compounds of interest. Note, though, that the focus of here is on the specific materials family we are proposing to be antiferroelectric; discussing in detail the high-throughput calculations, and further analysing the data obtained from them, would be the topic of a different publication.

Having said this, here are some details of our high-throughput calculations. We ran simulations for more than 50 non-magnetic perovskites. The list includes most I-V (e.g. $CsNbO_3$), II-IV (e.g. $SrHfO_3$) and III-III (e.g. $LaScO_3$) oxides (for the full list see the revised Suppl. Note 1). The key quantities (predictors) we tracked are the phonon instabilities at the zone centre and zone boundaries, that is, the eigenvalues and corresponding eigenvectors of the dynamical matrix at the Gamma, X, M and R points. From the more than 50 materials considered, not a single one presented a leading antipolar instability. Nevertheless, the three alkali vanadates of interest display strong antipolar instabilities of similar strength as the polar one. These details are now included in the Supplementary Note 1.

2) Why is molecular dynamics a good way of determining the ground state? Could a MD simulation not lead to the system being stuck in a local minimum and never reach the global minimum? Why did the authors not use standard structure prediction methods to explore configuration space more uniformly? Or perhaps enumerating symmetry-broken distortions? In this particular instance the predicted structure agrees with experiment, but is this approach generalizable when experiment is not available?

Once we identified the possible AFE candidates (namely the vanadates described in the text), our first approach was to try to condense the leading antipolar instability, and use the obtained structure as the starting point for a standard structural optimization with DFT. We then computed the phonons of the resulting structure. This typically led to further instabilities, so the process was iterated. This procedure will ultimately yield a minimum of the energy. Nevertheless, for the vanadates of interest here, this process turned out to be impractical due to the large number of steps needed to obtain a minimum. Further, it offers little guarantee that the obtained minimum is the global one. In hindsight, we note that this could have been expected from the fact that the instabilities in the cubic perovskite are very strong for the vanadates, indicating that this cubic phase is not a good reference structure.

To overcome these difficulties and explore configuration space in an unbiased way, we resorted to molecular dynamics (MDs) simulations at constant and very high temperatures (up to 1000 K), starting from the perovskite phase. A typical MD run would provide us with a collection of structures that we then used as starting points for a standard DFT structure optimizations. In essence, this should be tantamount to running repeated MD annealings, and is in fact quite similar to some of the structural-search algorithms most employed today [see e.g. Journal of Physics: Condensed Matter 23, 053201 (2011)]. Since in this process we obtained the experimentally reported ground state (which we noted after the fact, as we were not aware of this structure at the time we started the calculations), we stopped the search. Admittedly, to find the global minimum without any experimental information, it might have been advisable to validate our results by running additional structural searches, e.g. using evolutionary algorithms or particle swarm optimization. Yet, this did not seem necessary in the present case.

The procedure was not described in enough detail in the text, so we have extended the Methods section to correct this.

3) The studied vanadates turn out to be poor antiferroelectric candidates because the electric fields needed are too large. In the discussion, the authors qualitatively discuss a number of potential routes to perhaps make these or similar compounds work. Why did the authors not test these guesses?

We agree that the optimization routes discussed are worth pursuing, and in fact we are already working on some of them. Yet, we think it is important to publish the present article focused on one central general message: many common minerals are potential antiferroelectrics. The issue of optimization is a separate one, and in our opinion it makes more sense (and deserves) to be treated separately.

And some minor comments:

4) Typo: Fig. 3g should read Fig. 2g in the text.

The referee is right. We have corrected the typo.

5) The introduction mentions four vanadates, but $NaVO_3$ is not mentioned again. Why is that?

The referee is right in pointing this out. Referee #3 also asked about this, and we admit our presentation is not clear.

Our initial high-throughput calculations did point at $NaVO_3$ as a potential AFE candidate. Further, our structural relaxations yielded a lowest-energy phase with clear anti-polar features and, thus, potentially antiferroelectric. However, the obtained structure (which we checked coincides with the experimental one) is quite different from the ones presented here, and does not belong in the same discussion. Hence, we believe it does not make sense to discuss $NaVO_3$ in this article.

We have removed the mention to $NaVO_3$ in the introductory paragraph to avoid misunderstandings. We still mention it in the discussion, though, as a possible AFE candidate to be investigated in the future.

Reviewer #3 (Remarks to the Author):

The manuscript proposes a computational strategy to discover new possible antiferroelectric (AFE) material candidates, based on multiple density functional theory (DFT) methods including phonon calculations, ab-initio molecular dynamics (DF-MD) simulations, and nudged elastic band (NEB) calculations. The approach is applied to the alkali vanadates, where possible antiferroelectricity is demonstrated. The universality of the approach is further discussed with respect to compositions and for other compounds.

Overall, the results are novel, the study is technically thorough, and the manuscript reads well. Since the study could potentially motivate future computational and theoretical research towards exploring new AFE materials, it is of high interest to the ferroics research community. Thus, I think the manuscript fits the Communications Materials publication requirements well. I do, however, have some comments and concerns (remark 1-7) that must be addressed by the authors before I can recommend the manuscript for publication. I also have some minor comments and suggestions (remark 8-13) that might strengthen the manuscript and/or motivate further work. Please find my comments below.

1) On page 1 in the manuscript, it is stated that "alkali vanadates ($NaVO_3$, KVO_3, $RbVO_3$ and $CsVO_3$) show dominant and related polar and antipolar soft modes". While results for KVO_3, $RbVO_3$ and $CsVO_3$ are all reported, there are no results shown for $NaVO_3$. Either additional results for $NaVO_3$ must be added to the manuscript and/or the supplementary information, or it must be clearly justified why the results for $NaVO_3$ are omitted.

The referee is right in pointing this out, which Referee #2 mentions as well. We admit our presentation was not clear in this regard. Please see our response to point #5 from Referee #2.

2) On page 1 in the manuscript, it is stated that "first-principles molecular dynamics simulations ... reveal the existence of numerous low-energy metastable polymorphs". Are these polymorphs observed to be (meta)stable for all of the temperatures investigated (10 K to 1000 K), or only some of them? Do elevated temperatures induce any structural phase transitions between the polymorphs that might complicate the finite temperature AFE behavior discussed (e.g. in Fig 3)?

After reading the referees' reports we realised that the description of our procedure to obtain (meta)stable structures was not clear enough and may have been misleading. The ZZ, BM and RG (meta)stable structures were obtained after running short MD simulations at high temperature starting from the perovskite phase. A typical MD run would provide us with a collection of structures that we then used as starting points for a standard DFT structure optimizations. In this way, we were able to identify representative structures of the three types of chains/rings. We have extended the Methods section to clarify this point. (See also our response to comment #2 from Referee #2.)

Let us stress the following: We did *not* use MD simulations to check the stability of the discussed polymorphs at finite temperatures. They were merely a tool for structural discovery. We now use the term "phonon dispersion" instead of "dynamical stability" in the third paragraph of the introduction to avoid possible misunderstandings.

Having said this, our results do allow us to speculate about the thermal stability of the ground state ZZ-A. For example, from the energy barrier separating the ZZ-A and ZZ-F polymorphs, as calculated at zero applied electric field, we can estimate the temperature needed for the system to escape the ZZ-A minimum: we obtain ~ 1700 K (see Supplementary Note 2). Note that in the transition from ZZ-A to ZZ-F the main change in the structure is a rotation of tetrahedra that are only "fixed" at two corners, which is one of the most elementary and lowest-energy distortions to ZZ-A, as it leaves the VO_4 groups undistorted. Still, even this tilt is rather costly, which is the main reason why the obtained coercive fields are very large. Therefore, we do not expect transitions at temperatures below 1000 K, and believe that our analysis of the AFE hysteresis diagram of Fig.3 is sound as it is.

Note also that the disappearance of the electric dipoles associated to the VO_4 groups seems rather unlikely, since, as we mention in the discussion, the local dipoles will be present "by construction" as long as the VO_4 chains exist. In turn, the stability of the VO_4 tetrahedral groups is supported by the observed very large stiffness of the V—O bonds.

In this resubmission we have made sure to explain all these aspects in more detail, and thus avoid possible misunderstandings. We have also included a third Supplementary Video (Suppl. Video #1 in this resubmission) showing a typical MD simulation at constant temperature (in this case T=500 K) for the KVO_3 starting from the perovskite phase. The perovskite-like VO_6 groups break in the initial steps, quickly revealing the trend to form VO_4 tetrahedra chains.

3) Also in regard to the DF-MD simulations: In what order of magnitude are the trajectory lengths for the DF-MD calculations, and what time steps are used? In order to validate the claimed structural (meta)stabilities from the DF-MD calculations, typical trajectory lengths and the time steps in the DF-MD simulations must be included in the manuscript.

We would like to stress again that we are *not* using MD simulations to study the stability of the discussed phases. We have rephrased the sentence mentioning the "dynamical stability" to mention "phonon dispersion" instead in order to avoid possible misunderstandings. The MD calculations only served the purpose of exploring the configuration space initially and therefore the calculation details requested by the Referee should not be particularly relevant to the work described in our presentation.

4) On page 2 in the manuscript it is stated that "The ZZ structure is the most stable one, the lowest-energy BM and RG structures lying 117 meV and 125 meV per formula unit (f.u.)". It is not clear if these values are equal for all of the vanadates investigated or if they are from one specific model system and must be commented accordingly.

We have added "for KVO_3" explicitly in the main text to clarify this point.

5) The NEB path in Fig. 3(a) is extended up to "a FE state in which the polarization lies fully out-of-plane". As becomes apparent from the calculated MEP, and also addressed in the manuscript, this structure lies on a saddle point along the MEP. Is this FE structure structurally relaxed prior to the NEB calculation? I suspect that this structure is unstable and will relax back to the ZZ-F structure (or some other (meta)stable structure), unless this FE configuration itself is (highly) metastable?

It is indeed unstable, as the NEB analysis indicates. We obtained it by manually switching the VO_4 tetrahedra and then performing a standard symmetry-constrained structure optimization with DFT. It was therefore relaxed, but with imposed Pma2 symmetry, which guarantees the polarization is parallel to the *z* direction. If we had calculated the Hessian of this structure, we would have realized it is unstable (thus a saddle point) against a slight tilt of the VO_4 groups (and the development of an in-plane polarization component). This is indeed what the NEB revealed: the Pma2 structure is a saddle point and not a minimum of the energy. We still included it in the analysis because it presents a larger polarisation than the ZZ-F minimum, and could be relevant for measurements under applied electric fields.

In the revised version we have clarified how we obtain the final state in the NEB calculation and stressed it is indeed an unstable saddle point.

6) How did the authors calculate the polarization along the hysteresis-loops in Fig. 3(b) and Suppl. Fig. S2(b)-(e)? Is it extrapolated from the zero-field results assuming a linear dielectric response, and if so, which values of the dielectric constants (or dielectric susceptibilities) were used? This is unclear and must be explained in more detail.

The spontaneous polarization is computed using the modern theory of the polarization for each point (image) along the computed NEB path, which is obtained at zero applied field.

In the way we introduce the electric field, we are not treating the dielectric response in a quantitatively correct manner (we are missing the electronic response as well as part of the field-induced ionic response).

Regarding the hysteresis loop, the only values of the polarisation that we computed and are shown in Fig3b are those of the ZZ-A and the ZZ-F phases, and we indeed used the values obtained from the zero-field results. A small slope is drawn in the regions where there are no jumps to indicate that there is dielectric response in those regions and make the diagram more realistic, but that slope is not quantitatively relevant. We have clarified this the figure caption of Fig. 3 and in the main text, at the end of the paragraph describing Fig. 3b.

7) Regarding the methods section, the following essential details are missing and must be included or specified in the manuscript: - Which electrons where treated as valence electrons - or – Which specific PAW potentials supplied with VASP were used?

We thank the referee for pointing this out. We now explicitly state which electrons are treated as valence electrons within the PAW approach in the Methods section.

- What convergence criterion is used for the NEB calculations? Did the authors use the same criterion as for the structural relaxations (i.e. 0.01 eV/A)?

This was not clearly stated in the previous version of the manuscript, so we thank the referee for the comment. We now explicitly state in the NEB subsection of the methods that, indeed, the convergence criterion for the atomic forces in the NEB calculations was set to the same value as in the structural optimization calculations, 0.01 eV/Å.

- How long trajectories were typically calculated in the DF-MD simulations? (See also comment #3 above).

- What time step is used in the DF-MD calculations? (See also comment #3 above).

We have extended the Methods section explaining more clearly the approach we took to obtain the (meta)stable structures described in the manuscript. (See also answer to comment #3.) Therefore, we believe that both the trajectory length and time step of the MD simulations are not particularly relevant.

8) Is it possible to add a pseudo-cubic coordinate axis to Fig. 1 and to Suppl. Video #2, similar to those in Fig. 2? This will aid the reader to connect the structures in all the figures and videos to that of the perovskite structure in Fig. 1 (a). I would like to express my appreciation for the supplementary videos included, since they are very useful aids for the reader to clarify the phase transitions investigated.

We thank the referee for his/her comment and his/her appreciation of the videos. We have included the axes in Suppl. Video #2 (Supp Video #3 in this resubmission) as suggested, it indeed makes it easier to visualize and connect to the perovskite phase.

9) In Fig. 2 (e)-(f) it is difficult to distinguish the difference in the out-of-plane polarization component between the different structures, since the out-of-plane polarization is parallel to the view direction. Could the authors specify what the green and red arrows correspond to in the figure caption? Since the out-of-plane polarization is of the main interest in this study, it would be helpful to the reader to also include an illustration where the out-of-plane polarization component is perpendicular to the view direction to more clearly visualize the relative differences.

We thank the referee for pointing this out. The red and green arrows indicate dipoles with positive and negative out-of-plane component, respectively. We now indicate this in the caption for clarity.

We have also tried to make a figure in which the out-of-plane polarization is perpendicular to the point of view, but we have not succeeded in finding a point of view or setup in which the structure could be visualized more clearly. Still, we thank the referee for the suggestion.

11) Adding calculated electronic density of states (DOS) for the ZZ-A and ZZ-F polymorphs could be useful. While this is not the focus of the study, it will give proof that the materials investigated are electronically insulating, a prerequisite for (anti)ferroelectricity. Even though this is inferred by the calculated spontaneous polarizations, electronic DOSes will explicitly confirm this.

We thank the referee for the comment. We have included DOS calculations in the Supplementary Material (see Supplementary Note 4 and Supplementary Figure S4) for the three compounds (KVO_3, $RbVO_3$, $CsVO_3$) in the three relevant (meta)stable phases: ZZ-A, ZZ-F and ZZ-i. The results prove that these vanadates are insulating in all the studied phases.

12) It is a justified choice that the manuscript focuses mainly on the results of the ground state ZZ polymorph in KVO_3, as a proof-of-concept for the proposed AFE screening approach. While the following is beyond the scope of the manuscript, if the authors want to further extend the study, I would suggest to also include results for the AFE switching of the two other vanadate model systems investigated, similar to that reported for KVO_3 in Fig. 3 and Suppl. Fig. S2. This will add additional proof that the approach works for all the compounds investigated, and could strengthen the overall story.

The referee makes a good point. We decided not to present the full analysis for the three compounds for the sake of clarity in the message. Nevertheless, let us note that the details we deem most relevant regarding $RbVO_3$ and $CsVO_3$ are mentioned in the *discussion* section of the manuscript.

13) List of typos:
- On page 2 in the manuscript it is stated that "... the ZZ-F polymorph is shown schematically in Fig. 3g". The ZZ-F polymorph is shown in Fig. 2(g).

The typo has been corrected.

- On page 2 in the manuscript it is stated that "... an intermediate ferrielectric state (ZZ-i), with half of the tetrahedra in one of the chains flipped (Fig. 3f) ...". The ZZ-i polymorph is shown in Fig. 2(f).

The typo has been corrected.

Decision letter and referee reports: second round

11th Jun 20

Dear Prof Íñiguez,

Your manuscript titled "Antiferroelectricity in a family of pyroxene-like oxides with rich polymorphism" has now been seen again by referees #2 and #3, 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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We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

Dr Aldo Isidori

Associate Editor
Communications Materials

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

The changes provided by the authors are satisfactory.

Reviewer #3 (Remarks to the Author):

The authors have addressed all my previous comments satisfactorily. They have revised the manuscript and in the supplementary information accordingly, and any previous ambiguities regarding the proposed computational strategy should now be clear. I can recommend the manuscript for publication in Communications Materials in its current form.