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Decision letter and referee reports: first round

Date: 30th Oct 19

Dear Dr Asahi,

Thank you for submitting your manuscript, "Practical combinatorial chemistry boosted by materials informatics for accelerated discovery of superionic conductors", to Communications Materials. It has now been seen by 2 referees, whose comments are appended below. You will see that while they find your work of interest, they have raised 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.

In particular, you will see below that Referee 1 raises some issues with the methodology employed in the computational part of your study, and asks for some additional analysis. Should further data or analysis allow you to address these criticisms, we would be happy to look at a 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.

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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):

The authors proposed a high-throughput scheme to screen functional materials by combining the combinatorial chemistry and the materials informatics. Through this scheme, the oxide ion conductors in the chemical space of Ca-(Nb,Ta)-Bi-O were identified. The study focuses on an advanced research method in the materials science. The attempt of building new screening strategy have been discussed. However, the manuscript cannot be considered to publish unless the following questions can be clarified.

1. To solve the problem caused by limited number of supervised data, the authors adopted an additional criteria, the similarity of local structures between the candidate and the supervised data. In this work, the authors chose V7CuBi16O42 as the reference. However, as shown in Fig. 2a, most of the SOAP distances are larger than 0.6. If the authors chose another structure listed in Table S1 as the reference, other candidates will be selected. If there are enough supervised data chosen as references, most of the 48% structures of 13385 materials predicted by MI model will be selected. Then the criteria of similarity becomes meaningless. It is suggested that besides the similarity to V7CuBi16O42, the authors also give the information about the similarity to other supervised data. In this way, the readers can know the distribution of similarity in the whole data space, and can evaluate the effectiveness of this additional criteria.

2. In Fig. 2b, the frequencies of elements found in candidate materials are illustrated. The data are obtained from those with similar local structure to V7CuBi16O42 ($d<0.6$) and with high predicted conductivity ($\sigma>10\text{-}3$ S/cm). How about the frequencies of elements found in other area, e.g. $d<0.6$ and $\sigma<10\text{-}3$ S/cm? Will they show different distribution of elements? It will help the readers to understand whether the element distribution relates with the conductivity or not.

3. Since the parameter SOAP is selected as the screening criteria, the correlation between the SOAP and conductivity is suggested to be analyzed and presented in the manuscript.

4. In the part of combinatory synthesis and measurement, it is better to list all the conductivity data for each composition. The Fig 3, S3 and S4 provide the clear trend about how the ionic conductivities change along with the composition. But the specific data of the ionic conductivity (as well as other information like lattice parameters etc.) also valuable for researchers those want to study following this work.

In summary, more detailed information and sound data are needed to make the manuscript to be published.

Reviewer #2 (Remarks to the Author):

The authors clearly present a materials informatics technique to define a chemical search space for ionic conductors for use in SOFC's. They then apply this via a high throughput synthesis and characterization route to measure properties of identified samples. Importantly they follow this up with bulk samples to verify their thin film results.

The informatics technique and the identified compounds are all novel. As appropriate for this journal, The synthesis and characterization strategies are more completely detailed in their recent paper given as ref 22. (ACS Comb. Sci. 2019, 21, 400−407)

The paper will be of interest to those researching ionic conductors as well as to those in the general materials informatics field.

The claims are quite convincing as the informatics prediction is validated in thin film samples as well as in bulk samples.

I recommend the paper is suited for publication.

Author rebuttal letter: first round

Detailed response to reviewers' comments

[Manuscript ID: COMMSMAT-19-0029-T] "Practical combinatorial chemistry boosted by materials informatics for accelerated discovery of superionic conductors"

First of all, we would like to express great appreciation to all reviewers for their constructive comments. We have addressed each of their concerns as outlined below.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors proposed a high-throughput scheme to screen functional materials by combining the combinatorial chemistry and the materials informatics. Through this scheme, the oxide ion conductors in the chemical space of Ca-(Nb,Ta)-Bi-O were identified. The study focuses on an advanced research method in the materials science. The attempt of building new screening strategy have been discussed. However, the manuscript cannot be considered to publish unless the following questions can be clarified.

Answers for Review 1

We thank the reviewer 1 for the positive comments and the constructive questions which certainly improve our manuscript through clarifying each point of discussions as described below:

1. To solve the problem caused by limited number of supervised data, the authors adopted an additional criteria, the similarity of local structures between the candidate and the supervised data. In this work, the authors chose V7CuBi16O42 as the reference. However, as shown in Fig. 2a, most of the SOAP distances are larger than 0.6. If the authors chose another structure listed in Table S1 as the reference, other candidates will be selected. If there are enough supervised data chosen as references, most of the 48% structures of 13385 materials predicted by MI model will be selected. Then the criteria of similarity becomes meaningless. It is suggested that besides the similarity to V7CuBi16O42, the authors also give the information about the similarity to other supervised data. In this way, the readers can know the distribution of similarity in the whole data space, and can evaluate the effectiveness of this additional criteria.

It is true that if we select other good material as a reference for the SOAP distance, we

could find other elements to be recommended for the following combinatorial experiments. To illustrate this, we also selected $Bi_{1.5}Y_{0.5}O_3$, $La_3BiMo_4O_{18}$, and $Ce_{0.8}Sm_{0.2}O_{1.9}$ (or $Ce_{0.8}Gd_{0.2}O_{1.9}$) as reference materials for local structure similarity criterion, and examined which elements were included in the high conductivity materials ($\sigma > 10^{-3}$ S/cm). The results are illustrated in Fig. S7b-d in Supplementary Information. After eliminating toxic elements, noble metals, and 3d-transition metals, as similar to the case for $V_7CuBi_{16}O_{42}$, we list the elements of candidates as shown in Table S5. It can be seen that as the reference material differs, the selected elements also vary. This is a consequence that good conductivity can result from not a unique structure but some different local structures. In other words, taking a different reference, we have another chance to discover good materials. We have added these discussions in the last paragraph on page 4 in the revised manuscript, and in Sec. 4 in Supplementary Information.

2. In Fig. 2b, the frequencies of elements found in candidate materials are illustrated. The data are obtained from those with similar local structure to V7CuBi16O42 (d<0.6) and with high predicted conductivity (σ>10-3 S/cm). How about the frequencies of elements found in other area, e.g. d<0.6 and σ<10-3 S/cm? Will they show different distribution of elements? It will help the readers to understand whether the element distribution relates with the conductivity or not.

According to the reviewer's suggestion, we investigated the frequencies of elements found in the materials under following criteria; the SOAP distance for $V_7CuBi_{16}O_{42}$ is less than 0.6 ($d<0.6$) and the predicted conductivity at 973K is less than 10^{-3} S/cm ($\sigma<10^{-3}$ S/cm). The results are shown in the case 5 in Table S5 and Fig. S7e. The materials with lower conductivity include distinguishably Mg and Al instead of Nb and alkaline earth metals as in the case 1. Therefore, the discovery of m-BC phase (e.g., $Bi_{0.74}Ca_{0.26}O_{1.37}$) and its stabilization with Nb and Ta could not be achieved by the case 5. We also examined the frequencies of elements for the materials $\sigma<10^{-3}$ S/cm without any restriction of the SOAP distance as shown in the case 6 in Table S5 and Fig. S7f. A large frequency of Si appears in this case and suggests the local structure with respect to Si is not recommended by our approach. We have added these results in Sec. 4 in Supplementary Information.

3. Since the parameter SOAP is selected as the screening criteria, the correlation between the SOAP and conductivity is suggested to be analyzed and presented in the manuscript.

In this study, the SOAP distance is employed as a metric of the local structural similarity

to reduce a chemical space to be examined for the HT experiment. As we plot in Fig. 2a, this metric itself is not strongly correlated with conductivity. Of course, we can formulate a metric learning as a kernel regression model. In fact, we studied such a kernel regression model using the SOAP kernel, and observed a better prediction by adding other descriptors. Since the study is rather beyond the scope of the present work, we will present it in another publication in near future.

4. In the part of combinatory synthesis and measurement, it is better to list all the conductivity data for each composition. The Fig 3, S3 and S4 provide the clear trend about how the ionic conductivities change along with the composition. But the specific data of the ionic conductivity (as well as other information like lattice parameters etc.) also valuable for researchers those want to study following this work.

In response of the reviewer's suggestion, we added the list of the conductivity data for each composition of the HT library in Table S3 and the bulk samples in Table S4. For the compositions of the bulk samples, we also listed the lattice parameter of the main phase. The existence of these data can be suggested in the main text as well (in the second paragraph of page 5 and in the captions for Figs. 3 and 4).

In related to this revision, we found a small mistake in Figure 4a in the main text. In the previous version, we wrongly took the data for the library sample with z=0.6. We corrected the plot in the revised manuscript. We should note that any descriptions and conclusions in the manuscript are not changed with this revision (i.e., the chemical trend of the bulk samples was similar to that observed in the HT libraries). But we apologize for this mistake.

In summary, more detailed information and sound data are needed to make the manuscript to be published.

Reviewer #2 (Remarks to the Author):

Answers for Review 2

We thank the reviewer 2 for the positive comments and high evaluations to our work.

The authors clearly present a materials informatics technique to define a chemical search space for

ionic conductors for use in SOFC's. They then apply this via a high throughput synthesis and characterization route to measure properties of identified samples. Importantly they follow this up with bulk samples to verify their thin film results.

The informatics technique and the identified compounds are all novel. As appropriate for this journal, The synthesis and characterization strategies are more completely detailed in their recent paper given as ref 22. (ACS Comb. Sci. 2019, 21, 400−407)

The paper will be of interest to those researching ionic conductors as well as to those in the general materials informatics field.

The claims are quite convincing as the informatics prediction is validated in thin film samples as well as in bulk samples.

I recommend the paper is suited for publication.

Decision letter and referee reports: second round

Date: 17th Nov 19

Dear Dr Asahi,

Your manuscript titled "Practical combinatorial chemistry boosted by materials informatics for accelerated discovery of superionic conductors" has now been seen again by Reviewer 1, 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).

We therefore invite you to revise your paper one last time to address the remaining concerns of our reviewers. At the same time we ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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Title:
Identifying superionic conductors by materials informatics and high-throughput synthesis

Abstract:
Combinatorial chemistry has been proven effective in the search for novel functional materials, especially in the field of organic chemistry, and is being used to identify functional inorganic compounds. However, there is a growing need for approaches for predicting and experimentally realizing new materials, beyond compositional optimization of known systems. Application of combinatorial chemistry to materials discovery is typically hindered by a limited ability to search a wide chemical composition space, and by our ability to experimentally screen promising compounds. Here, a combinatorial scheme is proposed that combines a newly developed materials informatics technique to define a chemical search space with high-throughput synthesis and evaluation. We identify high-performance superionic conductors in the Ca-(Nb,Ta)-Bi-O system, demonstrating the effectiveness of this approach for accelerated materials discovery.

Please note that the title of the Supplementary Information will need to be updated also.

* Your paper must include the following headings: Introduction, Results (which can contain sub-headings), Discussion, Methods. A combined Results and Discussion section can be used, with sub-headings.

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"High-throughput prediction and synthesis are vital for obtaining new materials that deviate from existing compositions. Here, machine learning is combined with high-throughput synthesis to identify superionic conductors based on Ca-(Nb,Ta)-Bi-O."

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3b. If you don't yet have an ORCID account, you can easily create one by providing the required information and then clicking on 'Authorize'. This will link your newly created ORCID with your account on the MTS.

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The authors provided more detailed data and made further analysis. The paper is more valuable for the researchers in correlated fields. Thus, I suggest to accept the manuscript.