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Peer Review File

Evidence of underlying structural similarities of amorphous materials

Corresponding Author: Professor Akihiko Hirata

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

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Dear Professor Hirata,

Thank you for submitting your manuscript, "Evidence of underlying structural similarities of amorphous materials", 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, they have raised substantial concerns that must be addressed. In light of these comments, we cannot accept the manuscript for publication, but are interested in considering a revised version that addresses these serious concerns.

In particular, Reviewer 1 and 2 raise several concerns regarding the reliability of the findings. 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 response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response 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 a different 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):

This manuscript presents a fascinating study of structural similarities between amorphous metal oxides and metallic glasses, mainly focusing on the metal sublattice in amorphous HfO2 compared to Zr80Pt20 metallic glass. The authors used ABED and computational modeling to demonstrate that pentagonal bipyramids form a key structural feature in both material types. However, this article needs to be carefully considered for publication before the following doubts are clarified.
1. The explanation of structural similarity between amorphous HfO2 and Zr80Pt20 metallic glass is noteworthy, but it is somewhat exaggerated and does not address possible alternative explanations. The observed structural similarities may result from methodological artifacts (e.g., simulation parameters or limited sampling).
2. The manuscript states that 10 structural models of amorphous HfO2 were generated. The authors acknowledge that this number may be insufficient ("Although ten models are insufficient…"). Why were only 10 models generated, and how did the authors ensure the statistical representation of these models? Did the authors perform any statistical validation or variance analysis across these ten models? These raise concerns about the robustness and repeatability of the findings.
3. Do the observed diffraction spots from ABED patterns correspond to the diffraction from a single atom or represent an average result of multiple atoms within the beam interaction volume? If the spots arise from a single atom, how do the authors account for the inevitable vertical superposition of multiple Hf atoms within the 5 nm film thickness? On the other hand, if the spots are an averaged result from multiple atoms, how reliable is the interpretation of the pseudo-sixfold symmetry as an intrinsic property of the Hf sublattice? Could the observed symmetry arise from other sources, such as overlapping clusters, sample inhomogeneities, or alternative structural symmetries not considered in the analysis? The authors should provide experimental results of the ABED pattern from different directions to see if the fitting is still good or not.
4. The cooling rate in MD simulations (1 K/fs mentioned in Methods) is extremely fast compared to experimental cooling rates. How might this affect the structural features observed in the simulations? How do the authors justify their choice of cooling rates and densities in MD simulations, especially since such parameters are known to influence amorphous structures?
5. In Figure 2, the authors compare amorphous HfO2 with amorphous Si to highlight differences. However, SiO2 would be a more natural comparison as another oxide. Why wasn't amorphous SiO2 used as a comparison?
6. The manuscript assumes that the removal of oxygen atoms in the HfO2 model does not affect the structural conclusions. Still, this assumption may oversimplify the role of oxygen in stabilizing the Hf sublattice. How do the authors justify ignoring the influence of oxygen atoms in MRO/SRO characterization? Could the presence of oxygen affect the connectivity of atomic clusters?
7. The authors argue that the structural similarity between HfO2 and Zr80Pt20 metallic glass supports the universality of DRP structures. However, this conclusion may oversimplify the complexity of amorphous materials. Could the observed similarities simply reflect the high packing density of Hf and Zr atoms rather than a universal DRP structure? The authors claim the Hf atoms in amorphous oxides occupy positions similar to the DRP of hard spheres in metallic glasses. However, they should also explain the physical origin of this scenario. As Hf atoms are closely connected to O atoms, what is the driving force behind their packing themselves as DRP of hard spheres?
8. Although the authors demonstrate structural similarity, it is not exciting. Do these structural similarities imply potential similarities in physical or mechanical properties?
9. Line 118 “DRS of hard spheres” should be “DRP of hard spheres”.
In summary, the conclusions drawn are mostly consistent with the presented data; however, given the limited number of models and the qualitative comparison approach, the strength of certain conclusions may be overstated.

Reviewer #2 (Remarks to the Author):

The authors investigated the atomic structure of an ionic oxide glass (HfO2) at the medium-range order (MRO) scale using angstrom-beam electron diffraction (ABED) and ab initio and classical molecular dynamics (MD) simulations. To aid in the interpretation of their findings, they compared the atomic structure of the ionic glass with that of a metallic glass (Zr80Pt20) exhibiting certain MRO features.

The primary finding of this study is that the heavy atoms in the ionic glass exhibit a random dense packing configuration, which constitutes the characteristic MRO signature of the glass. From a theoretical standpoint, it is well established that the atomic structure of ionic glasses can be reasonably modeled using pair-additive potentials incorporating Coulomb

interactions, reflecting the strong ionicity of the system. This, in turn, implies that the atoms behave in a hard-sphere-like manner. In the case of the HfO_2 glass system, the Hf^{2+} cations exhibit a tendency toward dense random packing, suggesting that each Hf^{2+} cation is typically surrounded by 12–13 other Hf^{2+} cations due to the repulsive interactions. On the other hand, due to the requirement of charge neutrality, this subnetwork is expected to be distorted by the presence of O^{2-} anions. These anions are likely situated between pairs of Hf^{2+} cations or at the center of cationic polyhedra, depending on the degree of ionicity. Their presence leads to a shortening of the Hf–Hf distances, resulting in a distortion of the otherwise ordered icosahedral-like clusters. From this angle, the interpretation of the results seems logical to the reviewer.

A significant contribution of this work is the identification of a prominent structural motif: pseudo-six-fold bonding. Given the challenges in elucidating medium-range order structures in glasses, this study makes a valuable contribution to the field and merits publication. However, several aspects of both the experimental and simulation methodologies require clarification before the manuscript can be accepted. The following is a list of questions and concerns, presented in no particular order.

(1) The atomic structure of the HfO_2 glass derived from ab initio MD simulations should be validated or at least briefly described, as this is critical for assessing both the reliability of the model and the correct interpretation of the medium-range order (MRO). First, is the simulated structure of HfO_2 reliable given the current ab initio MD approach? A comparison with the experimental structure factor would be especially valuable in this regard. Additionally, regarding the short-range atomic arrangement, what is the average coordination number of O^{2-} anions around Hf cations? Is there any characteristic bond-angle distribution for the Hf–O–Hf triplets? These details are important for understanding the possible geometry of the observed sixfold Hf–Hf configurations, which may be mediated by bridging O^{2-} anions.

(2) Similarly, the simulation of the Si system requires further clarification. Under the reported cooling rate of 10^{12} K/s, it is likely that the resulting amorphous Si (a-Si) structure corresponds to a low-density amorphous state characterized by fourfold coordination. However, this has not been explicitly verified by the authors.

A more significant concern is the authors' claim that a medium-range order (MRO) structure was extracted from the atomic configuration. There is a lack of detail regarding how this MRO was identified, what methods were used, and what specific structural features define it. To the best of the reviewer's knowledge, the MRO in continuous random network (CRN) models of a-Si is not well established or clearly documented, and further elaboration is necessary to support this claim.

(3) It is also unclear why the authors selected elemental Si for the comparative study. Given the ionic nature of the HfO_2 system, a more appropriate analogue might be amorphous SiO_2, which shares similar characteristics such as network-forming behavior and the presence of bridging oxygen atoms. The rationale for using a-Si rather than a-SiO_2 should be clarified.

(4) While the authors report a prominent pseudo-sixfold feature observed in the ABED experiment (used partially to support their proposed docosahedral model of the ionic system), this raises a critical question: if fivefold bonding is expected to be the dominant structural motif, why was a distinct fivefold pattern not observed? In other words, what makes the sixfold feature stand out among all cluster symmetries?

Further details of the multislice ABED simulations are necessary to evaluate this point, including the cluster size used in the modeling. If discrete clusters were indeed employed, is there any specific relationship among the orientations of the sixfold bonds?

(5) Given that sixfold bonds can be interpreted as disclination lines, it is plausible that opposing arrangements of these bonds could enhance the overall sixfold symmetry within the clusters. Additional analysis in this direction would help to substantiate the authors' claim and clarify why sixfold symmetry emerges as the dominant feature.

Reviewer #3: See attached file.

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Version 1:

Decision Letter:

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Dear Professor Hirata,

Your manuscript titled "Evidence of underlying structural similarities of amorphous materials" 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.

We therefore invite you to revise your paper one last time to address the remaining concerns of Reviewer 2. At the same time we ask that you edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS
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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,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

I have carefully reviewed the authors' revised manuscript and their detailed responses to my comments. The authors have substantially addressed all major concerns I raised, particularly regarding statistical validation through large-scale classical MD simulations (324,000 atoms), clarification of ABED pattern interpretation, and inclusion of additional comparative materials (SiO2). The new data and analyses significantly strengthen their conclusions about structural similarities between amorphous metal oxides and metallic glasses. This work presents novel experimental evidence for a theoretically predicted phenomenon and provides valuable insights into the universal aspects of amorphous structures. I recommend this manuscript for publication.

Reviewer #2 (Remarks to the Author):

I have carefully reviewed the authors' replies to the reviewer's questions, and I am generally satisfied with their responses. The additional details provided for the simulations further solidify their conclusions, and I support the publication of the manuscript in Communications Materials.

There is one minor comment regarding the MRO identification of Si. I understand that the authors use the "MRO" feature (or lack thereof) to highlight the pseudo-six-fold symmetry in the HfO2 system. Nevertheless, this operationally obtained medium-range order (MRO) feature may not fully capture the true ordering in the medium range. Therefore, the use of MRO in this context should be carefully reconsidered and reworded.

Reviewer #3 (Remarks to the Author):

After reviewing the manuscript and the authors' response, I am pleased with the authors' clarifications and revisions. In my opinion, the manuscript is now suitable for publication.

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Replies to the comments of Reviewer #1:

This manuscript presents a fascinating study of structural similarities between amorphous metal oxides and metallic glasses, mainly focusing on the metal sublattice in amorphous HfO2 compared to Zr80Pt20 metallic glass. The authors used ABED and computational modeling to demonstrate that pentagonal bipyramids form a key structural feature in both material types. However, this article needs to be carefully considered for publication before the following doubts are clarified.

Reply: We sincerely thank the reviewer for carefully reading our manuscript. We appreciate the constructive feedback and address each of the specific comments below.

1. The explanation of structural similarity between amorphous HfO2 and Zr80Pt20 metallic glass is noteworthy, but it is somewhat exaggerated and does not address possible alternative explanations. The observed structural similarities may result from methodological artifacts (e.g., simulation parameters or limited sampling).

Reply: We appreciate the reviewer's thoughtful comments. To confirm that the observed structural similarities do not result from methodological artifacts, we have performed classical molecular dynamics simulations. Specifically, we have made 324,000-atom amorphous HfO_2 models at different cooling rates: 1.0×10^{15}, 1.0×10^{14}, and 1.0×10^{13} Ks^{-1}. Statistical analysis of variation across 10 samples at each cooling rate has confirmed that the docosahedral cluster is the dominant structural motif. In addition, our previous study [new Ref. [24]: Hirata, A. et al., Science 341, 376–379 (2013).] has also shown that the docosahedral structure is the most dominant in both a 200-atom *ab-initio* $Zr_{80}Pt_{20}$ model made at 4.0×10^{13} Ks^{-1} and a 12,000-atom classical $Zr_{80}Pt_{20}$ model made at 1.7×10^{10} Ks^{-1}. Since the results are independent of the method used (*ab initio* or classical, cooling rate, system size), the observed structural similarities are not methodological artifacts.

We have added the results of 324,000-atom amorphous HfO_2 models in the revised manuscript (new Fig. 1).

2. The manuscript states that 10 structural models of amorphous HfO2 were generated. The authors acknowledge that this number may be insufficient ("Although ten models are insufficient…"). Why were only 10 models generated, and how did the authors ensure the statistical representation of these models? Did the authors perform any statistical validation or variance analysis across these ten models? These raise concerns about the robustness and repeatability of the findings.

Reply: Due to the high computational cost of *ab initio* calculations, the analysis in the original manuscript was limited to 10 *ab initio* models, each with 324 atoms. To address this issue, we have performed classical molecular dynamics simulations, and their results

have been added in the revised manuscript (new Fig. 1). As we have explained in our reply to your comment #1, the statistical analysis of variation across 10 classical models, each with 324,000 atoms, has confirmed that the docosahedral cluster is the dominant structural motif.

3. Do the observed diffraction spots from ABED patterns correspond to the diffraction from a single atom or represent an average result of multiple atoms within the beam interaction volume? If the spots arise from a single atom, how do the authors account for the inevitable vertical superposition of multiple Hf atoms within the 5 nm film thickness? On the other hand, if the spots are an averaged result from multiple atoms, how reliable is the interpretation of the pseudo-sixfold symmetry as an intrinsic property of the Hf sublattice? Could the observed symmetry arise from other sources, such as overlapping clusters, sample inhomogeneities, or alternative structural symmetries not considered in the analysis? The authors should provide experimental results of the ABED pattern from different directions to see if the fitting is still good or not.

Reply: We appreciate the reviewer's thoughtful comments. We would like to clarify several points regarding the interpretation of angstrom-beam electron diffraction (ABED) patterns in our study. First, the observed ABED pattern reflects constructive interference among multiple atoms within the interaction volume of the electron beam, which in our experiment is approximately 1 nm in diameter and 5 nm in thickness. This is because a single atom cannot produce discrete diffraction peaks due to the absence of coherent interference. Second, due to the large difference in electron diffraction intensity between the Hf and O elements, the Hf atoms contribute predominantly to the ABED pattern, whereas the O atoms contribute negligibly (See also our reply to your comment #6). Thus, each of the observed ABED patterns reflects the arrangement of Hf atoms in a single medium-range order (MRO) region containing several clusters. Considering the probe size and film thickness, it does not reflect an average over larger-scale sample inhomogeneity.

To address the reviewer's concern about the directional dependence of the ABED pattern, we performed additional simulations using structure models of the identified MRO. We calculated ABED patterns from different viewing directions of the same MRO region (new supplementary Fig. 8). These simulations revealed that only one specific direction yields a pseudo-sixfold pattern, while other directions do not. This result strongly supports the conclusion that the observed symmetry arises from a specific projection of an anisotropic MRO, not from isotropic averaging or overlapping of randomly oriented clusters. Furthermore, to directly examine which atoms contribute to the sixfold periodicity, we performed a fast Fourier transform (FFT) analysis followed by inverse FFT filtering to extract the spatial frequencies corresponding to the observed sixfold pattern (new supplementary Fig. 11 and 12). The resulting inverse FFT image (in real space) clearly shows the Hf atom distribution responsible for the pattern. This

visualization confirms that the pseudo-sixfold symmetry originates from the internal arrangement of Hf atoms within a single MRO region. Finally, regarding the suggestion to experimentally obtain ABED patterns from different directions, we acknowledge that this would be ideal in principle. However, it is not technically feasible. In ABED experiments, tilting the sample inevitably shifts the illuminated region due to geometrical constraints and sample drift, making it impossible to maintain the same sub-nanometer region during rotation.

4. The cooling rate in MD simulations (1 K/fs mentioned in Methods) is extremely fast compared to experimental cooling rates. How might this affect the structural features observed in the simulations? How do the authors justify their choice of cooling rates and densities in MD simulations, especially since such parameters are known to influence amorphous structures?

Reply: To confirm that our conclusion is not affected by the choice of cooling rates, we have performed classical molecular dynamics simulations, and their results have been added in the revised manuscript (new Fig. 1). As we have mentioned in our reply to your comment #1, we have made amorphous HfO_2 models at cooling rates of 1.0×10^{15}, 1.0×10^{14}, and 1.0×10^{13} Ks^{-1}. It is found that the number of docosahedral clusters increases as the model is made more slowly. Therefore, our conclusion (the predominance of docosahedral clusters) is not affected by the choice of cooling rates.

5. In Figure 2, the authors compare amorphous HfO2 with amorphous Si to highlight differences. However, SiO2 would be a more natural comparison as another oxide. Why wasn't amorphous SiO2 used as a comparison?

Reply: Thank you for your comment. We would like to clarify why we selected amorphous Si for comparison. The comparison is to rule out the possibility that different structures can produce similar ABED patterns. This makes our claim more convincing because if different structures can produce similar ABED patterns, then similar ABED patterns do not necessarily indicate similar structures. We selected amorphous Si because its structure is obviously not DRP. This is precisely why amorphous Si is suitable for comparison. The ABED patterns obtained from amorphous Si and the additional amorphous SiO_2 (described below) have shown that different structures produce different ABED patterns, supporting our conclusion that the Hf sublattice and DRP are structurally similar. We have briefly described the reason why we selected amorphous Si in the revised manuscript (page 6, lines 175-177 and 183-188).

We agree that amorphous SiO_2 also warrants comparison. To address this, we additionally constructed an amorphous SiO_2 model using molecular dynamics simulation and analyzed its structure (new Supplementary Fig. 13). From this model, we selected clusters of similar size to the electron probe and calculated their diffraction (ABED)

patterns. We found several diffraction spots from SiO_2 at lower scattering angles (Q ~ 1.5 $Å^{-1}$) than from amorphous HfO_2 (Q ~ 2.3 $Å^{-1}$). This means that the MRO in SiO_2 has a longer real-space periodicity (d ~ 4.2 Å) than that in HfO_2 (d ~ 2.7 Å), which in turn indicates that SiO_2 and HfO_2 have different structural motifs.

6. The manuscript assumes that the removal of oxygen atoms in the HfO2 model does not affect the structural conclusions. Still, this assumption may oversimplify the role of oxygen in stabilizing the Hf sublattice. How do the authors justify ignoring the influence of oxygen atoms in MRO/SRO characterization? Could the presence of oxygen affect the connectivity of atomic clusters?

Reply: Thank you for your important comment. Our explanation may not have been clear enough, which might have led to some misunderstanding. Therefore, we would like to clarify the point. We did not examine the effects of O atoms on amorphous structure. The O atoms were removed to examine the contribution of O atoms to the ABED pattern of amorphous HfO_2. The arrangement of Hf atoms remains identical before and after the removal. We have mentioned this point in the revised manuscript (page 5, line 137). We note that the computed ABED patterns with and without oxygen are almost the same, which indicates that O atoms contribute negligibly to the ABDED pattern of amorphous HfO_2.

7. The authors argue that the structural similarity between HfO2 and Zr80Pt20 metallic glass supports the universality of DRP structures. However, this conclusion may oversimplify the complexity of amorphous materials. Could the observed similarities simply reflect the high packing density of Hf and Zr atoms rather than a universal DRP structure? The authors claim the Hf atoms in amorphous oxides occupy positions similar to the DRP of hard spheres in metallic glasses. However, they should also explain the physical origin of this scenario. As Hf atoms are closely connected to O atoms, what is the driving force behind their packing themselves as DRP of hard spheres?

Reply: We believe there might be a slight misunderstanding regarding the “universal dense random packing (DRP) structure. As the name suggests, the DRP structure of Hf atoms refers to a structure in which Hf atoms are densely packed. Although they are more accurately described as Hf ions, we refer to them as Hf atoms. The observed similarities reflect the high packing density of Hf and Zr atoms, which precisely characterizes the universal DRP structure

Because of the presence of oxygen, the structure of metals in amorphous metal oxides is generally not thought to resemble the dense random packing of hard spheres. However, our previous study has predicted this possibility [new Ref. 25: Nishio *et al*. *Phys. Rev. Lett.* **111**, 155502 1–4 (2013)], and the present experiments have supported it. The origin of the DRP structure of metal atoms in amorphous metal oxides can be

explained as follows. Since amorphous metal oxides are ionic solids, covalent bonding effects are not significant in determining their structure. Focusing on the metal sublattice, the primary role of oxygen atoms is to provide countercharges, and their effect can be approximated as a uniform background of negative charge. Therefore, the structure of the metal sublattice can be modeled by considering positively charged metal atoms embedded in a uniform negative background. As the structure of the metal sublattice is governed by spherical Coulomb repulsion, it adopts a DRP structure.

We have mentioned the origin of the DRP structure in the revised manuscript (page 9, lines 283-291).

8. Although the authors demonstrate structural similarity, it is not exciting. Do these structural similarities imply potential similarities in physical or mechanical properties?

Reply: Thank you for the comment. We understand the reviewer's concern that structural similarity alone may not be sufficient to generate broad interest unless it relates to relevant physical or mechanical properties. While we have not directly evaluated such properties in this study, to offer a possible connection from the perspective of glass-forming ability, we have added the following paragraph to the revised manuscript (page 8, lines 228-248).

The DRP of hard spheres crystallizes easily, because there are no energy barriers to crystallization[29]. Our analysis shows that amorphous HfO_2 and $Zr_{80}Pt_{20}$ are structurally similar to the DRP of hard spheres, whereas amorphous SiO_2 displays a distinctly different structure. SiO_2 is known to be an exceptional glass former, whereas HfO_2 and $Zr_{80}Pt_{20}$ exhibit more limited glass-forming ranges. This limitation can be explained as follows: due to their structural similarity to the DRP of hard spheres (docosahedral order), amorphous HfO_2 and $Zr_{80}Pt_{20}$ have low energy barriers to crystallization, resulting in their limited glass-forming ability. We point out that docosahedral clusters also predominate in the liquid and glass states of poor glass formers such as pure metallic glasses[29], argon[28], and $SmFe_{12}$[30]. The pseudo-sixfold symmetry arising from docosahedral clusters in the MRO structures of amorphous HfO_2 and $Zr_{80}Pt_{20}$ may also contribute to their limited glass-forming ability. We note that the absence of docosahedral clusters does not necessarily imply high glass forming ability. In fact, although amorphous Si is structurally different from the DRP of hard spheres, it has limited glass-forming ability. This limited glass-forming ability of Si arises from mechanisms that are not yet understood and differ from those related to structural similarity with the DRP of hard spheres. Although a comprehensive study of the relationship between structure and glass-forming ability is beyond the scope of the present work, our findings support the hypothesis that docosahedral order is an underlying factor that contributes to lowering glass-forming ability[30]. We believe these findings provide a potential direction for future investigation.

9. Line 118 "DRS of hard spheres" should be "DRP of hard spheres".

Reply: We have corrected the typo.

In summary, the conclusions drawn are mostly consistent with the presented data; however, given the limited number of models and the qualitative comparison approach, the strength of certain conclusions may be overstated.

Reply: We have carefully addressed the reviewer's concerns throughout our responses and the revised manuscript, and we believe that our clarifications and additional data appropriately support the conclusions.

Replies to the comments of Reviewer #2:

The authors investigated the atomic structure of an ionic oxide glass (HfO2) at the medium-range order (MRO) scale using angstrom-beam electron diffraction (ABED) and ab initio and classical molecular dynamics (MD) simulations. To aid in the interpretation of their findings, they compared the atomic structure of the ionic glass with that of a metallic glass (Zr80Pt20) exhibiting certain MRO features.

The primary finding of this study is that the heavy atoms in the ionic glass exhibit a random dense packing configuration, which constitutes the characteristic MRO signature of the glass. From a theoretical standpoint, it is well established that the atomic structure of ionic glasses can be reasonably modeled using pair-additive potentials incorporating Coulomb interactions, reflecting the strong ionicity of the system. This, in turn, implies that the atoms behave in a hard-sphere-like manner. In the case of the HfO_2 glass system, the Hf^{2+} cations exhibit a tendency toward dense random packing, suggesting that each Hf^{2+} cation is typically surrounded by 12–13 other Hf^{2+} cations due to the repulsive interactions. On the other hand, due to the requirement of charge neutrality, this subnetwork is expected to be distorted by the presence of O^{2-} anions. These anions are likely situated between pairs of Hf^{2+} cations or at the center of cationic polyhedra, depending on the degree of ionicity. Their presence leads to a shortening of the Hf–Hf distances, resulting in a distortion of the otherwise ordered icosahedral-like clusters. From this angle, the interpretation of the results seems logical to the reviewer.

A significant contribution of this work is the identification of a prominent structural motif: pseudo-six-fold bonding. Given the challenges in elucidating medium-range order structures in glasses, this study makes a valuable contribution to the field and merits publication. However, several aspects of both the experimental and simulation

methodologies require clarification before the manuscript can be accepted. The following is a list of questions and concerns, presented in no particular order.

Reply: We thank the reviewer for the careful reading of our manuscript and for the constructive feedback. We address the comments and concerns point by point below.

(1) The atomic structure of the HfO_2 glass derived from ab initio MD simulations should be validated or at least briefly described, as this is critical for assessing both the reliability of the model and the correct interpretation of the medium-range order (MRO). First, is the simulated structure of HfO_2 reliable given the current ab initio MD approach? A comparison with the experimental structure factor would be especially valuable in this regard. Additionally, regarding the short-range atomic arrangement, what is the average coordination number of O^{2-} anions around Hf cations? Is there any characteristic bond-angle distribution for the Hf–O–Hf triplets? These details are important for understanding the possible geometry of the observed sixfold Hf–Hf configurations, which may be mediated by bridging O^{2-} anions.

Reply: Thank you for this important comment. To assess the reliability of the *ab initio* molecular dynamics (AIMD) model of amorphous HfO_2, we calculated the X-ray structure factor from the simulated structure and compared it with experimental data reported in the literature [new Ref. [14]: L. C. Gallington *et. al.*, Materials 10, 1290 (2017)]. The results show good agreement, which supports the validity of the structural model (new Supplementary Fig 1).

L. C. Gallington *et. al.* showed that the average number of O atoms around an Hf atom is 6.8, the peak position in the pair distribution function corresponding to Hf-O bonds is 2.13 Å, and the peak positions corresponding to Hf-Hf bonds are 3.38 and 3.89 Å. Our corresponding *ab initio* MD results are as follows: the average number of O atoms around an Hf atom is 6.6, the peak corresponding to Hf-O bonds is located at 2.07 Å, and the peaks corresponding to Hf-Hf bonds are located at 3.35 and 3.75 Å. Our results agree with the experimental data. We have also calculated the Hf-O-Hf bond angle distribution function, which shows peaks at 102° and 129°. These results agree with the classical molecular dynamics results by L. C. Gallington et. al., who reported peaks at 102°and 135°. These results are shown in new Supplementary Figs. 2 and 3.

(2) Similarly, the simulation of the Si system requires further clarification. Under the reported cooling rate of 10^{12} K/s, it is likely that the resulting amorphous Si (a-Si) structure corresponds to a low-density amorphous state characterized by fourfold coordination. However, this has not been explicitly verified by the authors. A more significant concern is the authors' claim that a medium-range order (MRO) structure was extracted from the atomic configuration. There is a lack of detail regarding how this MRO was identified, what methods were used, and what specific structural features define it.

To the best of the reviewer's knowledge, the MRO in continuous random network (CRN) models of a-Si is not well established or clearly documented, and further elaboration is necessary to support this claim.

Reply: We thank the reviewer for this important and detailed comment. In response, we would like to clarify two points: the structural characteristics of the amorphous Si model, and our approach to identifying medium-range order (MRO). First, we have confirmed that our a-Si model shows predominantly fourfold coordination, as expected for a continuous random network. Specifically, the coordination analysis reveals that 88.3% of Si atoms are fourfold coordinated, 11.5% are fivefold, and 0.2% are sixfold. This supports the idea that the model is composed mainly of tetrahedrally bonded Si atoms, consistent with low-density amorphous Si produced by rapid quenching. This explanation has been added to the caption of new Fig. 3.

Second, rather than applying a fixed topological definition of medium-range order (MRO), we adopted an operational definition inspired by the spatial resolution of ABED. Specifically, we selected atomic clusters of approximately 1 nm in size, comparable to the electron probe, and calculated their diffraction (ABED) patterns. If a cluster exhibited strong and discrete diffraction spots, we interpreted this as evidence of structural coherence beyond the short-range scale (i.e., the presence of MRO). This method emphasizes an experimentally motivated operational definition of MRO, reflecting what would be detectable in ABED measurements. While it does not impose a predefined geometric or topological criterion, we believe this approach provides a physically meaningful and experimentally relevant way to identify medium-range order.

(3) It is also unclear why the authors selected elemental Si for the comparative study. Given the ionic nature of the HfO_2 system, a more appropriate analogue might be amorphous SiO_2, which shares similar characteristics such as network-forming behavior and the presence of bridging oxygen atoms. The rationale for using a-Si rather than a-SiO_2 should be clarified.

Reply: Thank you for your comment. We would like to clarify why we selected amorphous Si for comparison. The comparison is to rule out the possibility that different structures can produce similar ABED patterns. This makes our claim more convincing because if different structures can produce similar ABED patterns, then similar ABED patterns do not necessarily indicate similar structures. We selected amorphous Si because its structure is obviously not DRP. This is precisely why amorphous Si is suitable for comparison. The ABED patterns obtained from amorphous Si and the additional amorphous SiO_2 (described below) have shown that different structures produce different ABED patterns, supporting our conclusion that the Hf sublattice and DRP are structurally similar. We have briefly described the reason why we selected amorphous Si in the revised manuscript (page 6, lines 175-177 and 183-188).

We agree that amorphous SiO_2 also warrants comparison. To address this, we additionally constructed an amorphous SiO_2 model using molecular dynamics simulation and analyzed its structure (new Supplementary Fig. 13). From this model, we selected clusters of similar size to the electron probe and calculated their diffraction (ABED) patterns. We found several diffraction spots from SiO_2 at lower scattering angles ($Q \sim 1.5$ $Å^{-1}$) than from amorphous HfO_2 ($Q \sim 2.3$ $Å^{-1}$). This means that the MRO in SiO_2 has a longer real-space periodicity ($d \sim 4.2$ Å) than that in HfO_2 ($d \sim 2.7$ Å), which in turn indicates that SiO_2 and HfO_2 have different structural motifs.

(4) While the authors report a prominent pseudo-sixfold feature observed in the ABED experiment (used partially to support their proposed docosahedral model of the ionic system), this raises a critical question: if fivefold bonding is expected to be the dominant structural motif, why was a distinct fivefold pattern not observed? In other words, what makes the sixfold feature stand out among all cluster symmetries? Further details of the multislice ABED simulations are necessary to evaluate this point, including the cluster size used in the modeling. If discrete clusters were indeed employed, is there any specific relationship among the orientations of the sixfold bonds?

Reply: While we may not have fully grasped your concerns mentioned in your comment #4, we believe that the core of the comment lies in why the pentagonal structural units result in a quasi-hexagonal pattern instead of a pentagonal one. The absence of a pentagonal pattern is due to the incoherent orientation of pentagonal structural units. Our previous study has shown that even in the case of a single icosahedral cluster, a pentagonal pattern may not appear depending on the incident angle of the electron beam [new Ref. [24]: Hirata, A. et al., Science 341, 376–379 (2013).]. To clarify the origin of the pseudo-hexagonal ABED pattern, we performed a fast Fourier transform (FFT) analysis of the Hf atomic configuration in the MRO region. We then applied inverse FFT (IFFT) filtering using only the six strongest spots that form the pseudo-hexagonal pattern in reciprocal space (Supplementary Figs. 11 and 12). Our results show that the origin of the pseudo-sixfold ABED pattern is the formation of the pseudo-triangular lattice seen in the IFFT image. While some atoms contribute to its formation, others do not. However, as a whole, the projections of the atoms in the pentagonal bipyramids form the distorted triangular lattice. The orientation and the distortion of pentagonal bipyramids appear to facilitate its formation. We have mentioned these points in the revised manuscript (page 6, lines 160-174).

(5) Given that sixfold bonds can be interpreted as disclination lines, it is plausible that opposing arrangements of these bonds could enhance the overall sixfold symmetry within the clusters. Additional analysis in this direction would help to substantiate the authors' claim and clarify why sixfold symmetry emerges as the dominant feature.

Reply: While we may not have fully grasped your comment #5, we believe that the core of this comment lies in why the pentagonal structural units result in a quasi-hexagonal pattern instead of a pentagonal one. Since we have clarified this point in our reply to your comment #4, we believe that your comment #5 has also been addressed.

Replies to the comments of Reviewer #3

This paper investigates the structural similarities between amorphous metal oxides and metallic glasses by employing sub-nanometer beam electron diffraction. The research is anchored in a theoretical framework that challenges the common perception that amorphous metal oxides are generally perceived to differ structurally from metallic glasses, due to their dense packing of hard spheres. The experimental findings presented in this study indicate that the hafnium sublattice in amorphous hafnia displays distorted icosahedral (decosahedral) structures, similar to those observed in the Zr80Pt20 metallic glass, when compared with simulated models. This timely investigation addresses a significant topic in the realm of amorphous materials, particularly concerning metallic glasses. The authors utilize their extensive experience in structure determination through nano-beam electron diffraction, thereby increasing our understanding of the structural characteristics of amorphous metal oxides. Overall, the manuscript is well-articulated and demonstrates a high level of expertise, representing a noteworthy contribution to the literature that has the potential to become seminal with revisions.
Prior to publication the authors should address the following points:

Reply: We thank the reviewer for the thoughtful summary and positive evaluation of our work. We appreciate the encouraging comments and address the specific points raised below.

1. Line 23: Following the statement "Understanding the fundamental structural features of amorphous ...," I recommend incorporating a reference from Y. Yang et al. (Nature 592 (2021) 60-64) to provide a solid foundation for your argument.

Reply: Thank you for the suggestion. We have added the recommended reference in the revised manuscript.

2. Lines 24-27: It would be beneficial to specify that the structural differences between amorphous metal oxides and metallic glasses originate from the differing types of bonding—metallic versus covalent—since this distinction is central to your discussion.

Reply: Thank you for the helpful suggestion. We have revised the sentence to clarify that the structural differences arise from the different types of bonding. The revised sentence

is “Because of the different types of bonding, such as ionic, metallic, and covalent, amorphous metal oxides are generally thought to be structurally different from metallic glasses. While amorphous metal oxides consist of metal atoms surrounded by oxygen atoms, metallic glasses resemble the dense random packing (DRP) of hard spheres.” (page 1, lines 24-28)

3. Lines 65-73: The current focus on the Hf sublattice comes across as somewhat convoluted. I suggest rephrasing this section and aligning it with the insights provided in line 127 to enhance coherence.

Reply: Thank you for the suggestion. We are not entirely sure what the intention of this comment is. Is the referee suggesting that the sentence structure of the explanation regarding the Hf sublattice is overly complex? In lines 65–73 of the original manuscript, we explain the rationale for choosing the Hf sublattice and the outline of this work, and in line 127 of the original manuscript, we state that the choice of the Hf sublattice works effectively. We do not fully understand why these parts may have come across as convoluted. If the referee could kindly provide more specific guidance on what should be revised, we would be happy to make the necessary improvements.

4. Lines 103-114: When defining MRO, it is critical to clarify how the clusters are interconnected to effectively occupy three-dimensional space. Ref. [8] demonstrated that for Zr84Pt16, solute-centred clusters exhibit significant icosahedral topological order termed ‘icosahedral ordering.’ Additionally, they identified a second type of building unit, characterized as ‘strings,’ formed by the connectivity of solute atoms. Differentiating these structures from those found in Ref. [8] would greatly enhance your analysis.

Reply: Thank you for raising this important point. In the Hf sublattice, the distinction between solute and solvent is not meaningful. If a distinction must be made, the Hf atoms correspond to the solvent species. In addition, the Zr-centered clusters in $Zr_{80}Pt_{20}$ are solvent centered clusters. Accordingly, our focus is on the arrangement of solvent-centered clusters, in contrast to Ref. [8], where the arrangement of solute-centered clusters is studied. We also point out that the structure of $Zr_{80}Pt_{20}$ glass is similar to that of pure metallic glass, which in turn resembles the DRP of identical hard spheres but differs from it in some respects. The deviation is most apparent in solute-centered clusters. In fact, Pt-centered clusters tend to form an icosahedral structure rather than a docosahedral one. Therefore, analyzing solute-center clusters effectively highlights the structural differences. However, because solvent atoms constitute the majority, the overall structure of $Zr_{80}Pt_{20}$ glass remains similar to that of the DRP structure. Studying solvent-centered clusters emphasizes this structural similarity. This point has been discussed in the discussion section of the new manuscript (page 8, lines 249-259).

5. Cavities: You may discuss the presence of cavities resulting from the packing arrangements of clusters, as this could align with Bernal's classical notion of canonical holes when considering clusters as hard spheres.

Reply: Thank you for the insightful comment. As suggested, we have examined the presence of cavities from a topological perspective using persistent homology. Specifically, we computed the second persistence diagrams (PD2) for the Hf sublattice in amorphous HfO_2 and for the atomic configuration of $Zr_{80}Pt_{20}$. These PD2 results capture topologically persistent voids, which correspond to the concept of canonical holes proposed by Bernal. Interestingly, both systems exhibit similar distributions in their PD2, suggesting a structural similarity in terms of void topology. We believe this finding provides a modern topological interpretation of Bernal's canonical holes and further supports the analogy between the two amorphous structures. A brief explanation (page 7 lines 216-225) and corresponding figure (Supplementary Fig. 15) have been added in the revised manuscript.

6. Lines 159-160: Regarding the MD simulation of Zr80Pt20, Ref. [14] offers experimental data on this composition. I would recommend addressing why this data was not utilized for comparative analysis in your study.

Reply: Thank you for pointing this out. We acknowledge that our previous paper (Ref. [14], new Ref. [24]) includes ABED data for $Zr_{80}Pt_{20}$. However, the data in Ref. [14] were obtained using a different convergence lens aperture and were primarily aimed at characterizing short-range order (SRO) structures. In contrast, our current study focuses on medium-range order (MRO), and the experimental conditions were specifically optimized to probe these features. Because of this difference in experimental setup and structural focus, we believe that a direct comparison with the data from Ref. [14] is not straightforward. For this reason, we chose not to include it in the present manuscript.

7. Line 309: An EDS analysis confirming the composition of hafnia should be included in Supplementary Fig. 4 to verify the chemistry.

Reply: Thank you for your suggestion. We have added the EDS result to Supplementary Fig. 9, as requested. The analysis confirms an O/Hf ratio of 2.18, which is close to the ideal stoichiometry of HfO_2. Considering the known limitations of EDS for light elements such as oxygen, especially when compared with heavy elements like hafnium, we believe that this result is consistent with the expected composition.

8. Line 318: Please clarify how the probe size was determined. Was it accomplished by fitting a Gaussian function to the FWHM of the intensity profiles captured on a camera?

Reply: Thank you for your comment. We agree that the probe size is an important parameter in the interpretation of ABED data. In this study, the ABED measurement was performed in STEM mode, and we were not able to directly image the actual beam profile during the experiment. Direct measurement proved to be technically difficult, even after consultation with the microscope manufacturer (JEOL). Instead, we estimated the probe size based on a combination of experimental tests and simulations. Specifically, we used a different convergence lens aperture (5 μm), for which beam imaging was possible using a crystalline sample, and then extrapolated the probe size for the 3.5 μm aperture used in this study by comparing the optical parameters through beam simulations. Since the full procedure is somewhat complicated and technical, we chose not to include the detailed process in the manuscript. However, we believe the estimation is reasonable for the purpose of this study.

9. Lines 370 and onwards: It is advisable to emphasize that the docosahedral structure as a special case of distorted icosahedral structure is the central figure for describing the local structure since previous Voronoi index analyses have neglected the significance of docosahedral structures due to their inability to differentiate polyhedral types (Voronoi indices of (0,3,6,4)).

Reply: We greatly appreciate your understanding of the significance of the docosahedral structure. We have added the sentence "This research has also broadened the applicability of the emerging idea that the dodecahedral structure is a central figure for describing the local structure of a wide range of amorphous materials[28-30]." to the conclusion section (page 10, lines 297-299). In addition, we have added the following paragraph to the discussion section (page 9, lines 260-282). Since there appears to be a slight misunderstanding, we have clarified this point at the end of the paragraph.

Concerning the docosahedral order, we note that our previous study[29] has demonstrated the following. In the DRP of hard spheres, the most frequently observed Voronoi index is ⟨0, 3, 6, 4⟩. However, this does not necessarily imply that the corresponding structures are physically meaningful. The high frequency of ⟨0, 3, 6, 4⟩ arises simply because the Voronoi index method does not distinguish between Voronoi polyhedra with different graph structures. In contrast, the most frequently observed p_3 code is @4$(56)^2 5^8$, which represents the docosahedral structure. The predominance of the docosahedral structure can be explained as follows. At the length scale of clusters formed by an atom and its neighboring atoms, a regular icosahedral cluster provides the highest local packing density. However, there are inherent gaps between the atoms of the regular icosahedral cluster. When some of these gaps are reduced through local rearrangements, other gaps are inevitably enlarged. Since an additional atom fits into one of these enlarged gaps, a dodecahedral cluster is formed. Since the docosahedral cluster and the icosahedral cluster share structural similarities, the docosahedral cluster is often referred to as a distorted icosahedral cluster. However, the phrase "distorted icosahedral cluster" implies

that it is a member of the icosahedral cluster. In contrast, the docosahedron is a 22-faced polyhedron, not a 20-faced one. Therefore, calling the docosahedral cluster a distorted icosahedral cluster constitutes a category error. Terms such as “icosahedral-like cluster” are more appropriate when drawing analogies between the docosahedral and icosahedral clusters. However, in the context of dense random packing, the docosahedral cluster is a key structural feature. Therefore, it is not reasonable to refer to the docosahedral cluster as an icosahedral-like cluster. If anything, the icosahedral cluster is a docosahedral-like cluster.

10. Question on HAADF image: Concerning the dark contrast features in the HAADF images presented in Supplementary Fig. 4, are these variations attributable to differences in density or foil thickness?

Reply: Thank you for your observation. It is not straightforward to determine the exact origin of the dark contrast features in the HAADF images. As the reviewer suggests, variations in density or foil thickness are both plausible explanations. We agree that these are likely contributing factors. In particular, since the film was prepared by sputtering, it is possible that island-like structures were formed during the initial stages of deposition. Considering that the total film thickness is very thin (approximately 5 nm), such initial non-uniformity could lead to local thickness variations. Although we cannot definitively identify the origin of the contrast variation, we consider that local fluctuations in thickness are the most probable cause in this case.

Response to the comments of reviewer 2:

I have carefully reviewed the authors' replies to the reviewer's questions, and I am generally satisfied with their responses. The additional details provided for the simulations further solidify their conclusions, and I support the publication of the manuscript in Communications Materials.

Reply: We sincerely thank the reviewer for taking the time to carefully read our revised manuscript and detailed responses. We greatly appreciate the reviewer's supportive comments and are grateful for the recommendation to publish our work in Communications Materials.

There is one minor comment regarding the MRO identification of Si. I understand that the authors use the "MRO" feature (or lack thereof) to highlight the pseudo-six-fold symmetry in the HfO2 system. Nevertheless, this operationally obtained medium-range order (MRO) feature may not fully capture the true ordering in the medium range. Therefore, the use of MRO in this context should be carefully reconsidered and reworded.

Reply: As pointed out by the reviewer, the structural motifs extracted from our amorphous Si model do not necessarily represent medium-range order (MRO). Therefore, we have replaced the term "MRO structure" with "local structure" in the manuscript. We believe that this change will help avoid any misunderstanding that the structures used in our ABED calculations directly correspond to MRO in amorphous Si. In addition, to clarify our intention, we have added the following sentence to the manuscript: "Since the concept of MRO in amorphous Si has not yet been generally established, we avoid using the term MRO for Si in this study."

The revised portions are shown as they appear in the main text and caption.

[Main text (line 175)]

To validate our structural interpretation, we ruled out the possibility that distinct structures could yield similar ABED patterns. To this end, we first examined amorphous Si. This material has an open structure composed of tetrahedrally bonded Si atoms, which is different from the DRP structure[4,36,37]. From the structure model of amorphous Si calculated by MD (Fig. 3a), we extracted ~~an MRO~~ a local structure (Fig. 3b) and simulated the ABED pattern by rotating the ~~MRO~~ structural model (Fig. 3c). Since the concept of MRO in amorphous Si has not yet been generally established, we avoid using the term MRO for Si in this study. The simulated ABED pattern obtained from a certain orientation exhibits a pseudo-sixfold symmetry. However, unlike HfO_2 (Fig. 3d), additional diffraction spots, indicated by red circles, were observed at a lower scattering angle region. Thus, it was found that the ABED pattern of a continuous random network is distinct from that of the DRP-like configuration. A similar result was also obtained from an

ABED pattern of amorphous SiO_2 (Supplementary Fig. 13 and Fig. 14). These results support our argument that the agreement between the experimental ABED pattern of amorphous HfO_2 and the simulated ABED pattern indicates that the Hf sublattice has a DRP-like structure.

[Caption (line324)]

Fig.3 Atomic configuration and diffraction of amorphous Si. a, Amorphous Si model simulated using molecular dynamics, together with a Si tetrahedral unit shown in the inset. The coordination analysis reveals that 88.3% of Si atoms are fourfold coordinated, 11.5% are fivefold, and 0.2% are sixfold, indicating that the model is composed mainly of tetrahedrally bonded Si atoms, consistent with low-density amorphous Si produced by rapid quenching. b, ~~MRO~~ Local structure extracted from the model shown in a. c, Simulated ABED pattern of the ~~MRO~~ structural model shown in b. d, Experimental ABED pattern of amorphous HfO_2 as a reference.