Universal geometric frustration in pyrochlores

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Materials with the pyrochlore/fluorite structure have diverse technological applications, from magnetism to nuclear waste disposal. Here we report the observation of structural instability present in the pyrochlores $A_2Zr_2O_6O^\prime$ ($A =$ Pr, La) and $Yb_2Ti_2O_6O^\prime$, that exists despite ideal stoichiometry, ideal cation-ordering, the absence of lone pair effects, and a lack of magnetic order. Though these materials appear to have good long-range order, local structure probes find displacements, of the order of 0.01 nm, within the pyrochlore framework. The pattern of displacements of the $A_2O^\prime$ sublattice mimics the entropically-driven fluxional motions characteristic of and well-known in the silica mineral $\beta$-cristobalite. The universality of such displacements within the pyrochlore structure adds to the known structural diversity and explains the extreme sensitivity to composition found in quantum spin ices and the lack of ferroelectric behavior in pyrochlores.
from catalysis, ferroelectricity, luminescence, magnetism, and even nuclear waste storage, compounds which crystallize in the pyrochlore structure are utilized for countless applications. This makes knowledge of the structural flexibility of the pyrochlore structure, $A_2B_2O_7$, a derivative of the fluorite structure, crucial. The structure contains interpenetrating, corner-sharing $O_A^+$ and $O_B^+$ tetrahedra, shown in Fig. 1a. $A$ is typically a larger (~0.1 nm) cation while $B$ is a smaller cation (~0.05 nm), where the central $O^-$ site is unoccupied.

Stoichiometric flexibility is common for the pyrochlore structure, such as in $Y_2Nb_2O_7$ ($Y_2(Y_{1.4}Nb_{0.6})_2O_9$), which contains both an $A$ cation on the $B$ site and $O$ vacancies. Additional disorder, such as $A/B$ site-mixing is not uncommon, and can lead to the websterite structure, unless optimal cation ordering occurs. Lastly, polyhedral distortions can also occur, where the tetrahedral corners move in or out. If in/out displacements have long-range order then the global symmetry drops from $Fd\overline{3}m$ to $F\overline{4}3m$ evidenced by the addition of 2h 0 0 reflections, as seen for $Pb_2Ru_2O_9$ due to a combination of lone pair effects and off-stoichiometry. In-out ordering only exists over short-length scales, it is equivalent to 2-in-2-out ($2120$) ordering, which is expected to be disordered on long-length scales due to degenerate configurations. This is observed for Nb-pyrochlores due to charge disproportionation, and also for $Y_2Mo_2O_7$ observed as split peaks in X-ray absorption spectroscopy. Though this disorder is often not magnetically driven, for pyrochlores with magnetic cations, it is this same short-range order which contains larger displacements and is more disordered.

An alternative type of disorder, cooperative tetrahedral tilting, also exists for compounds such as $Bi_2Ti_2O_7$ and $Bi_2Ru_2O_7$, and is attributed to lone-pair effects. Ferroelectric behavior is expected from this disorder, though these materials are only dielectrics with ferroelectric behavior attributed to impurities. Better understanding this type of disorder is essential to describe why these pyrochlores are not ferroelectric, despite the local structure deviating from cubic symmetry, as well as understanding why so few pyrochlores are ferroelectrics despite having large dielectric constants.

Here we provide evidence for this disorder in the pyrochlores Pr$_2$Zr$_2$O$_7$ (PZO), La$_2$Zr$_2$O$_7$ (LZO), and Yb$_2$Ti$_2$O$_7$ (YTO), due to static $A$ and $O$ displacements (see Fig. 1c). These displacements mimic isoreticular $\beta$-cristobalite, where corner-sharing tetrahedra cooperatively tilt, allowing for an increase in the Si–O bond length and a deviation of the O–Si–O angle from 180° (see Fig. 1d). The displacements lower the local symmetry to $P4_212_2$ and exist here despite ideal cation ordering, ideal stoichiometry, the absence of lone pair effects, and despite LZO being nonmagnetic. Powder diffraction and selected area electron diffraction (SAED) hint at structural disorder, where pair distribution function (PDF) analysis refinements prefer static, rather than thermally dynamic, displacements. Additionally, $^{91}$Zr NQR on a PZO series indicate an inhomogeneous bonding environment of Zr as a function of $A/B$ cation ratio, while high-angle annular dark field scanning transmission electron microscopy (HAADF STEM) reveals a static displacement of ~0.01 nm for $A$ and $O$. Though previous works have observed similar displacements and the associated structural frustration, we generalize that these static displacements are common in pyrochlore structures and are driven by cation size mismatch, rather than defect concentrations or electronic effects.

Results
Diffraction data. Rietveld refinements of powder X-ray and neutron diffraction on a single crystal of LZO display neither the $\{200\}$ reflection nor any secondary phases (see Supplementary Figure 1). Refinements used anisotropic displacement parameters (ADP), yielding anisotropic displacement ellipsoids (ADE) such as those shown in Fig. 1b. Details of X-ray diffraction on PZO and YTO are found in refs. respectively. All $A$-site cations have pancake-like ADE, suggesting tetrahedron tilting, rather than the rod-like ADE indicative of in/out ordering. Systematic refinement tests were conducted for PZO, LZO, and YTO for off-stoichiometry, cation site-mixing, or O off-stoichiometry and each test indicated the absence of these effects (see Supplementary Discussion for more details). This allows us to conclude that the stoichiometry and occupancies are within 0.5% of nominal values (see Supplementary Figures 2–28), and indicates unambiguously that these materials are nearly defect free.

Additional tests were conducted for evidence of structural displacements, by placing the $A$ and $B$ cations on the $32e(x x x)$, $96h:(0 y y)$ and $96c(z x x)$ Wyckoff positions. Pr, Zr, La, and Yb all showed an equal preference for the $96c$ and $96h$ sites, and Ti showed only a preference for the $32e$ site. To obtain reliable information about O displacements, similar tests were conducted using neutron diffraction data, confirming that La and Zr prefer the $96c$/$96d$ sites, O prefers the $96g$ site, and O$^-$ does not move. Though alternative Wyckoff positions (static ordering) improve refinement statistics, this improvement was not statistically significant from fits with ADP (dynamic ordering). This analysis merely suggests displacements are static, which would have significant impacts on both magnetic and ferroelectric behavior.

Intensity on the allowed $\{442\}$ reflection would suggest a static $\beta$-cristobalite disorder due to $A$, $B$, or O displacements. Although none of the powder diffraction data have intensity on the $\{442\}$ reflection, Supplementary Figure 1a demonstrates that
Supplementary Figures 29, 41). These displacements are consistent with a robust O dislocation, a correction due to disordered static displacements which alleviate La–O bond lengthening. This required collecting the SAED patterns in Fig. 2 off-center of the main reflections to avoid irreversibly damaging the detector. Due to this, reflections from the First Order Laue Zone are observed as well. This pattern of weak diffuse streaks is associated with \( \beta \)-cristobalite disorder, due to SiO\(_4\) tetrahedral rotations and Si–O bond lengthening. The same diffuse scattering has also previously been observed for LZO, and was hypothesized to be due to disordered static displacements which alleviate La–O' over bonding. However, the diffuse scattering could indicate preferential dynamic motion instead. In comparison with previous works, our materials have ideal stoichiometry, are nearly defect free, and the magnitude of the displacements appears smaller, hence harder to observe, and thus required longer exposure times even though faint diffuse scattering exists at shorter exposure times (see Supplementary Figures 42, 43). If the displacements are static, it implies local disorder, suggesting frustrated, rather than cooperative, tetrahedral tilting, which would perturb long-range magnetic or ferroelectric order.

**Local structure probes.** To further understand the local structure, and hence the effects on physical properties, neutron PDF (NPDF) was collected on PZO and X-ray PDF (XPDF) data was collected on YTO (see Fig. 3). Fits with purely isotropic displacement parameters were not sufficient to describe the data, while fits with ADP better describe the data (see Fig. 3a, d – \( R_w = 11.70 \text{ vs. } R_w = 9.09 \) and \( R_w = 10.50 \text{ vs. } R_w = 9.56 \)), but are still imperfect, especially at short distances (\( r < 0.35 \text{ nm} \)).

Systematic refinement tests for alternative Wyckoff positions yielded 0.013(2) nm 96g/96h Pr displacements, 0.004(2) nm 96g/96h Zr displacements, 0.0103(2) nm 96g O displacements, and a robust O' position for PZO; also, yielding 0.0098(9) nm Yb 96g/96h displacements, 0.0113(3) nm Ti 32e displacements, 0.0154(4) nm 96g O displacements, and a robust O' position for YTO (see Supplementary Figures 29, 41). These displacements are consistent with a \( \beta \)-cristobalite distortion, modeled in Fig. 3b, c, e, f with refinements in \( P_{412_12} \) symmetry (details in Supplementary Tables 1, 2).

A \( P_{412_12} \) refinement improves fit statistics (\( R_w = 9.09 \text{ vs. } R_w = 8.76 \) for PZO and \( R_w = 9.53 \text{ vs. } R_w = 8.68 \) for YTO), and visual inspection of Fig. 3b, e shows improvements in the region of the A–O and A–O bond lengths (\( r < 0.35 \text{ nm} \)). Refinements using a range of \( Q_{\text{max}} \) values produced equivalent fits, and refinements with similar degrees of freedom also preferred a static \( P_{412_12} \) model. These lower symmetry refinements, which are quantitatively and qualitatively preferred, model only several A–O'/A–O distances, rather than a large collection of distances modeled by higher symmetry refinements with ADPs. However, Fig. 3c, f demonstrate that this static model remains imperfect from 0.35 nm < \( r < 0.60 \text{ nm} \), and only slightly improves modeling at longer distances (\( r > 0.60 \text{ nm} \)). This implies that the local symmetry is lowered due to static displacements in each O' tetrahedra (\( r < 0.35 \text{ nm} \)), more disorder exists between tetrahedra (0.35 nm < \( r < 0.60 \text{ nm} \)), and that a locally disordered model accurately describes the long-range ordered structure. Further, the increased A–O'/A–O bond distances which lower the local symmetry, would suggest frustrated, rather than cooperative, motion between tetrahedra, interrupting any long-range ordered states.

\( \beta \)-Zr NQR is shown in Fig. 4 for a series of sintered powder PZO samples. Only one peak is observed, as expected for the ideal structure, though the breadth of the peak increases systematically as \( x \) decreases in \( Pr_{2+\text{x}}Zr_{2-x}O_7-x/2 \). The broad
and non-symmetric peak shape indicates that the electric field gradient (EFG) around $^{91}\text{Zr}$ is not homogeneous for $x = 0$ and $x = -0.02$. This behavior is only expected if the compound has discrete structural displacements (slower than $\approx 10^{-7}$ s, from Fig. 4) and the three-fold rotation symmetry around the [111] crystallographic axis is locally perturbed. Notably, the same asymmetric peak broadening has been observed for $^{89}\text{Y}$ NMR on Y$_2$Mo$_3$O$_7$, attributed to inequivalent Y sites at lower temperature$^{29}$. Given that observation, peak asymmetry is expected when $x = -0.02$, as some Zr is on the Pr site would have a drastically different bonding environment. When $x = 0$ and the material is stoichiometric, the EFG for Zr is still not symmetric, suggesting non-uniform next-nearest neighbor distances. Finally, when $x = +0.02$, the Zr bonding environment appears more uniform, indicating that the EFG around $^{91}\text{Zr}$ becomes more homogeneous as the larger Pr is placed on the smaller Zr site, suggesting effects of the A/B cation size ratio.

If these displacements are static, then a shift from the $Fd\bar{3}m$ Wyckoff positions should be observable in HAADF STEM. If the displacements are purely dynamic, then the average position should remain the same even if the dynamic motion is anisotropic. In contrast to the timescales due to atomic interactions ($=10^{-12}$–$10^{-15}$ s), HAADF STEM is a long timescale measurement, of the order of seconds, much longer than the timescale expected for dynamic motion (at most $=10^{-6}$–$10^{-12}$ s). The longer timescale and increased resolution makes HAADF STEM ideal for distinguishing between fluctuations around an ideal position (dynamic) and averaged positions that are displaced from the ideal (static).

Figure 5a shows a HAADF STEM image for PZO oriented in the [110] direction. During data collection the structure appeared

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**Fig. 3** Neutron and X-ray Pair Distribution Function analyses on Pr$_2$Zr$_2$O$_7$ and Yb$_2$Ti$_2$O$_7$, respectively. Time-of-flight neutron PDF for Pr$_2$Zr$_2$O$_7$ refinements focusing on a and b short length scales and c longer length scales. Synchrotron X-ray PDF for Yb$_2$Ti$_2$O$_7$ focusing on d and e short length scales and f longer length scales. Refinements for the ideal model (isotropic displacement parameters) are shown in green, and non-symmetric peak shape indicates that the electric field gradient (EFG) around $^{91}\text{Zr}$ is not homogeneous for $x = 0$ and $x = -0.02$. This behavior is only expected if the compound has discrete structural displacements (slower than $\approx 10^{-7}$ s, from Fig. 4) and the three-fold rotation symmetry around the [111] crystallographic axis is locally perturbed. Notably, the same asymmetric peak broadening has been observed for $^{89}\text{Y}$ NMR on Y$_2$Mo$_3$O$_7$, attributed to inequivalent Y sites at lower temperature$^{29}$. Given that observation, peak asymmetry is expected when $x = -0.02$, as some Zr is on the Pr site would have a drastically different bonding environment. When $x = 0$ and the material is stoichiometric, the EFG for Zr is still not symmetric, suggesting non-uniform next-nearest neighbor distances. Finally, when $x = +0.02$, the Zr bonding environment appears more uniform, indicating that the EFG around $^{91}\text{Zr}$ becomes more homogeneous as the larger Pr is placed on the smaller Zr site, suggesting effects of the A/B cation size ratio.

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**Fig. 4** $^{91}\text{Zr}$ Nuclear Quadrupole Resonance data for the series Pr$_{2+x}$Zr$_{2-x}$O$_7$. Experimental data is shown as red squares ($x = 0.02$), black circles ($x = 0$), and blue triangles ($x = -0.02$). Solid lines represent Lorentzian fits with respective full-width half maxima (FWHM) shown. Lorentzian fits are poorer for $x = 0$ and $x = -0.02$ due to asymmetric peak shapes. Size of the symbols represents standard uncertainties given by the scatter of the baseline.
regular and no noticeable defects (including anti-site phase boundaries) were observed, as exemplified by representative zoomed out images (Supplementary Figures 44, 45). Figure 5a shows a corresponding electron energy loss spectroscopy (EELS) elemental map where red represents Pr, blue represents Zr, and purple represents mixed columns (see Methods section for processing details, and Supplementary Figures 46, 47 for representative images). The contrast of this map across the field of view is in close agreement with the expected A/B cation ordering, as indicated from Rietveld refinement tests. Determining precise atomic column composition from on-axis EELS data is known to be challenging due to beam propagation effects and the quantification of atomically-resolved EELS data would normally require a careful comparison with inelastic image simulations\(^3\) or a relatively complex inversion process\(^\text{31}\). Nevertheless, in contrast to a recent report for off-stoichiometric Yb\(_2\)Ti\(_2\)O\(_7\) samples where significant site mixing could be observed visually even in unprocessed maps\(^\text{32}\), the uniformity of the map shown in Fig. 5a seems to be in close agreement with the lack of chemical disorder.

Rather than attempting to quantify the EELS results in terms of column composition, intensity profiles from HAADF images were instead examined to attempt to estimate the uniformity of the observed Z-contrast. Figure 5b displays the average profile intensities for each of the two row types (mixed and alternating columns) of PZO oriented in the [110] direction, with the individual row intensities displayed in Supplementary Figure 48. Given that powder diffraction and PDF refinements indicate no site-mixing or off-stoichiometry, we assume that site mixing is a negligible contribution in rows with mixed cations columns; instead, the standard deviation of mixed column rows accounts for experimental deviations of intensity (due to counting statistics). Figure 5b demonstrates that there is no significant deviation from ideal cation ordering, as the average profile intensity maxima all fall within one standard deviation of each other. Analyzing the individual row intensities, it is seen that only 0.83% (1/120) atomic columns deviate from ideal cation ordering. Using the proposed binomial distribution model\(^\text{34}\), even assuming this column contains two defects, only suggests a stuffing defect concentration of 0.11%, well below the 0.5% limit as indicated by powder diffraction and PDF refinements (see SI for details), further indicating that the crystals are nearly defect free.

To look for static displacements of the order of 0.01 nm, a high precision workflow (see SI for details) was used to acquire representative HAADF images, following which the script Ranger was used to identify the coordinates of the atomic columns from the resulting high-resolution scanning transmission electron microscopy (HRSTEM) images\(^\text{33}\), while ideal atomic positions were calculated from the \(\text{Fd}\_3\text{m}\) structure for comparison. Figure 6a shows the results of this analysis on PZO oriented in a [111] direction, with displacement vectors (black arrows) shown between ideal (black circles) and experimental (red triangles) positions. Utilizing the difference between a sub-pixel 2-D Gaussian refined experimental positions\(^\text{33}\) and an ideal pyrochlore structure, the averaged displacements of [111] atomic columns are observed to be 0.013(6) nm, which are markedly larger than the precision typically achieved with this workflow (consecutive acquisition followed by rigid or non-rigid registration) with this instrument\(^\text{34}\), and is in phenomenal agreement with NPDF refinements (0.013(2) nm). The displacements in the [111] orientation appear to be in moderate agreement with those expected from the PZO NPDF refinements (overlaid on Fig. 6a), while agreement in the [110] direction is poorer (see Supplementary Figure 49).

The larger mismatch between the static \(\text{P}_4\_2\_2\_2\) model and PZO [110] STEM image (see Supplementary Figure 49a) is not unexpected given the disorder indicated by the SAED patterns in Fig. 2. Along the [110] direction the atomic columns highlight the corners of the tetrahedra, whose positions are driven by the distortion in neighboring tetrahedra. The low connectivity, combined with competing degenerate \(\beta\)-cristobalite displacements, creates geometric frustration, which leads to entropic disorder of the \(\beta\)-cristobalite structure between tetrahedra (0.35 nm < r < 0.60 nm) as suggested by the XPDF and NPDF analyses. This again indicates the tetrahedra tilting is frustrated rather than cooperative.

The tetrahedra connectivity in each orientation is important, as a single unit cell can have four single atom types in the [110] direction, and only one single atom type in the [111] direction. This explains why the PZO [110] orientation is more sensitive to tetrahedra–tetrahedra disorder and has more imperfect agreement between the PZO NPDF model and HRSTEM images. However, our PDF analysis indicates that the expected length scale of order is only <0.35 nm, smaller than the thickness of the HAADF STEM samples. For this reason, it is surprising that any
displacement can be observed in this way, even though it is a statistically real value, and may indicate that the structure is more ordered than anticipated in the [111] direction. To prove the validity of the observed displacement, we further this analysis by comparing the rows in two separate [111] images, taken at different locations on the same sample, with the expected pattern of displacements for the $\beta$-cristobalite structure.

A histogram of distances between atoms in each row, taken from multiple images (Fig. 6a and Supplementary Figure 50), is shown in Fig. 6b. Careful observation of comparisons between simulated and PDF refined structures, shown in Fig. 6c, d, respectively, demonstrates that Pr shifts either all left or right in one row (1), and alternating left and right in the next row (2). Binning these rows separately, using the median and standard deviation (across 153 atomic columns) to create the bin locations and width, Fig. 6b demonstrates one set of rows (1) retains a small distribution around a single distance while the other rows (2) have two maxima, indicating Pr displaces in alternating directions, as expected for a $\beta$-cristobalite displacement in this orientation (as shown in Fig. 6c, d). Additionally, this histogram displays the 0.01 nm deviation from ideal positions, a result well

| Table 1 Summary of experimental results |
|---------------------------------------|
| Technique | $\delta$ (nm) |
|---------------------------|---------------|
| **Pr$_2$Zr$_2$O$_7$** |                      |
| SAED         | N/A           |
| SXPD         | Pr-0.011(2)   |
| NPDF*        | Pr-0.013(2)   |
| HRTEM*       | Pr-0.013(6)   |
| 9$^1$Z NQR*  | N/A           |
| SAED         | N/A           |
| XPD          | Yb-0.0123(18) |
| XPDF*        | Yb-0.0098(9)  |
| Pr           | Tr-0.011(3)   |
| **Yb$_2$Ti$_2$O$_7$** |            |
| SAED         | N/A           |
| XPD          | Yb-0.0123(18) |
| NPDF          | Yb-0.0098(9)  |
| Pr           | Tr-0.011(3)   |
| **La$_2$Zr$_2$O$_7$** |          |
| SAED         | N/A           |
| XPD          | La-0.0094(16) |
| NPDF          | La-0.0079(15) |
| Pr           | O-0.0054(13)  |

Techniques with an asterisk (*) denotes a methodology which confirms displacements are static with local disorder, rather than dynamic motion. Errors represent statistical uncertainties. SAED selected area electron diffraction, SXPD synchrotron X-ray powder diffraction, NPDF neutron pair distribution function, XPDF X-ray pair distribution function, XPD laboratory X-ray powder diffraction, and NPD neutron powder diffraction.
within error of the cation displacements indicated by PXD, PND, XPDF, and NPDF refinements, and further validates the frustrated tilting of the O′A4 tetrahedra due to the elongation of the O′-A bond.

**Discussion**

To understand our results, summarized in Table 1, we need to understand the origin of these displacements. One obvious reason for these displacements is electronic ordering. The β-cristobalite distortion could be caused by a Jahn-Teller effect, where either the central or surrounding atoms could be displaced. Though displacements due to Jahn-Teller effects are typically first-order due to mixing of partially filled d orbitals, dβ transition metals are also known to undergo second-order Jahn-Teller displacements due to mixing of filled p and empty d orbitals35, 36, and displacements of B in the BO3 octahedra would in-turn displace the surrounding O and A cation. If the displacements observed here are an effect of dβ cations, then only pyrochlores with dβ transition metals could be affected. However, Ti prefers the 8a site (2120 displacements) while Zr, which has a larger cation radius than all the other tetrahedra, would prefer the 96g/96h site (β-cristobalite displacements). This observation might indicate that second-order Jahn-Teller displacements prefer in-out rather than β-cristobalite type displacements. Knowing the symmetry of the mixing p and d orbitals would help resolve this, as the symmetry of the displacement must match the symmetry of the mixing HOMO and LUMO bands36.

Another obvious reason for these displacements is inherent strain, well known to exist in the pyrochlore structure5, 23, 37–40. The fluorite structure, which resembles the pyrochlore structure when A and B cation sizes are similar and equally mixed, follows body center cubic packing. The pyrochlore structure similarly follows face center cubic packing, but the B4 tetrahedra are smaller than the O′A4 tetrahedra. For large A/B ionic radii ratios, the size of the O′A4 tetrahedra are constricted in size by the smaller B4 tetrahedra. Much like β-cristobalite, the tetrahedra distort, allowing longer A–O′ bond distances, which relieve the constrained O′A4 tetrahedra, and displace the surrounding O. If this is the case, then β-cristobalite disorder would be present in all pyrochlores with larger A/B ionic radii ratios.

Tabira, Withers et al. have observed diffuse scattering for myriad zircanate and titanate pyrochlores5, indicative of β-cristobalite distortions27, proposing that tetrahedral distortions occur in non-magnetic La2Zr2O7O′ to relieve La–O′ over-bonding22. In contrast to previous work, we additionally rule out the effects of impurity elements, site mixing or stuffing, and off-stoichiometry, by analyzing crystals grown as part of series, whose physical properties match those of stoichiometric powders23, 24, further confirmed by Rietveld and PDF refinements. Given that our work also concludes that the diffuse scattering is due to static, rather than dynamic, displacements, we generalize that if these displacements are due to A/B cation size mismatch, then static displacements exist in all zircanates and titanates at the very least. EXAFS investigations on the ruthenate Pr2Ru2O7 likewise found evidence for Pr disorder and deviations in the Pr–O′ bonding41. These types of displacements may even explain the structural details for other pyrochlores as well, such as Y disorder in the recently contested Y2Mo2O711, 23, 29 or the disorder observed in hafnates42. If this is the case, then these static displacements, which exist at room temperature, have a significant impact on the properties of these materials.

This structural disorder adds to the number of entropic possibilities at low temperatures. In geometrically and magnetically frustrated compounds, like pyrochlores, this would induce a large array of degenerate magnetically ordered states, creating many zero-gap or small gap equivalent ground states, and preventing such a material from reaching a theoretical ground state. This does not necessitate that frustration is magnetically driven; rather our results suggest that the frustration is structurally driven with significant impacts on the magnetic ordering, enhancing spin-liquid behavior and at the very least creating spin-glass behavior. Such effects have recently been observed43, 44, and are important for understanding the underlying physics of the spin-ice state. More thoroughly, a β-cristobalite distortion may not significantly alter bond distances, but bond angles, such as A–O–A, change drastically, and next-nearest neighbor distances are altered even more dramatically. Hence these small changes in bond distances have extremely large effects on magnetic interactions, explaining why 1–2% changes in stoichiometry have drastic changes in magnetic susceptibility and heat capacity for pyrochlores43, 45.

Likewise, this also explains why 2% level adjustments in the cation stoichiometry of PZO toward excess Pr leads to a sharper 91/Zr NQR line. As the larger Pr is placed on the smaller Zr site, it allows for the Pr4 tetrahedra to expand without distorting, creating more uniform next-nearest neighbor distances. This suggests a design principle of tuning the stoichiometry of these materials to obtain desired properties.

Curiously, ideal stoichiometry leads to optimal magnetic ordering, despite non-uniform magnetic interactions. For instance, any deviation away from nominal stoichiometry in Yb2Ti2O7 lowers the temperature of the transition seen in heat capacity data24 as placing the smaller Ti on Yb sites (stuffing) requires the O′Yb4 tetrahedra to expand less while placing the larger Yb on the smaller Ti sites (anti-stuffing) allows the OYb4 tetrahedra to expand without distorting, creating more uniform next-nearest neighbor distances. In both situations, more uniform magnetic interactions should exist, but for both stuffing and anti-stuffing the transition temperature and magnitude of the heat capacity significantly decreases24. This indicates that these delicate magnetically ordered states, which already contain magnetic disorder, are easily interrupted by either a lack of magnetic cations on the A-framework, or extra magnetic cations on the B-framework. Site-mixing would additionally interrupt the delicately magnetically ordered degeneracies, suggesting that ideal magnetic order in pyrochlores cannot exist without non-uniform magnetic interactions.

Signatures of this disorder should be readily observable in spectroscopic measurements, arising as a continuum of non-magnetic, temperature independent, low energy excitations. Resonant inelastic X-ray scattering has observed such a feature for Eu2Ir2O7, Pr2Ir2O7, and Sm2Ir2O728, 46, though its appearance is likely complicated by other excitations. This feature unexpectedly extends to higher energy for Pr2Ir2O7 than Eu2Ir2O7, as a result of the larger cationic ratio of Pr/Ir, inducing more disorder for Pr2Ir2O7. Similarly, because the local symmetry is lowered, higher energy excitations would also appear – though their intensities would be severely diminished based on the magnitude of the displacements, as is the intensity of the allowed {442} reflection for diffraction data.

Though space group P43212 may not accurately describe the disorder between tetrahedra, it is the highest symmetry space group which allows for tetrahedra to rotate in all three directions, and conveniently contains only one symmetry-equivalent A and B cation. Similarly, the disorder due to frustrated tilting of the tetrahedra, prevents the pyrochlore structure from being ferroelectric, despite the local structure deviating from cubic symmetry. It is this same local disorder which prevents these materials from ordering in their ferroelectric ground state16, 18 that also enhances the dielectric properties. This lattice frustration has been previously proposed, though only in the context of lone-pair active cations with large displacements43. Our results
generalize that hypothesis to likely include all pyrochlores, even when they contain minimal defects, which emphasizes that frustrated tetrahedral motion is the defect-free pyrochlore ground state. The inherent geometric frustration of the pyrochlore structure necessitates that the displacements, and hence dipoles, point in different directions, canceling each other out over a single, or several, unit cells. This behavior prevents displace spontaneous polarization such as for perovskites BaTiO$_3$ or PbTiO$_3$, but enhances dielectric behavior due to small, localized electric dipoles. Given enough disorder to relieve the geometric frustration, i.e. O vacancies and A/B site mixing, long-range order and ferroelectric behavior might be recovered and is likely the origin of ferroelectric behavior in materials such as Cd$_3$Na$_2$O$_7$ and Pb$_4$NdO$_7$.$^{19}$

Though the diverse variety of techniques herein, with multiple complementary techniques applied to Pr$_2$Zr$_2$O$_7$, La$_2$Zr$_2$O$_7$, and Yb$_2$Ti$_2$O$_7$, show both indirect and direct evidence for a static displacement in pyrochlores in the absence of any type of defects or electronic effects, further experiments, which look at atomic positions as a function of temperature, would prove even more conclusively that this displacement is static, and not dynamic. However, if these displacements are due to A/B cation size mismatch they exist in all pyrochlores and not only resolve several long standing issues, such as the discrepancy between experimental and calculated pyrochlore lattice parameters.$^{5, 48-51}$ but also many recently contested issues$^{11, 25, 42}$.

Since the spontaneous polarization such as for perovskites BaTiO$_3$ or PbTiO$_3$, show both indirect and direct evidence for a static displacement in pyrochlores in the absence of any type of defects or electronic effects, further experiments, which look at atomic positions as a function of temperature, would prove even more conclusively that this displacement is static, and not dynamic. However, if these displacements are due to A/B cation size mismatch they exist in all pyrochlores and not only resolve several long standing issues, such as the discrepancy between experimental and calculated pyrochlore lattice parameters.$^{5, 48-51}$ but also many recently contested issues$^{11, 25, 42}$.

### Methods

**Synthesis.** Stoichiometric single crystals of LZO, PZO, and YTO were prepared by the optical floating zone method.$^{23}$ Growth conditions were individually optimized to produce homogenous single crystals with physical properties indistinguishable from stoichiometric polycrystalline samples. LZO was prepared by grinding stoichiometric amounts of La$_2$O$_3$ (99.99%, Alfa Aesar) and ZrO$_2$ (99.978%, Alfa Aesar), after they were individually dried overnight at 1000°C. Large sample masses were used to minimize mass error (± 20 g) and final oxygen content was corrected by heating in ambient atmosphere. Ground, mixed precursors were placed into an alumina crucible and heated under ambient atmosphere to 1350°C for 12 h. Upon further heat treatments at 1500°C for 40 h, with intermediate grindings and pelleting, powder X-ray diffraction confirmed phase purity.

Polycrystalline feed rods made from the powder were then sintered at 1500°C in a four mirror image furnace (Crystal System Inc.). Polycrystalline feed rods made from the powder were then sintered at 1500°C in a four mirror image furnace (Crystal System Inc.).

**Diffraction.** Laboratory powder X-ray diffraction patterns were collected for ground single crystals of PZO, LZO, and YTO single crystals, oriented down the [111] direction, using a Phillips CM300 FEG TEM, operating at an accelerating voltage of 297 kV. Off-center images were collected on an Orius CCD camera, while centered images were collected on film (Kodak SO 163). Patterns were collected under a large variety of exposure times (10–100 min) to determine the best exposure time to highlight the diffuse scattering, as demonstrated by Supplementary Figures 42, 43. Additional intensity scaling tricks, such as changing image brightness/contrast and inverting the colors, were used. A beam stop was not used both because the X-ray exposure times still remained in beam spilling, and to observe the completeness of the diffuse scattering.

**Electron microscopy.** Selected area electron diffraction (SAED) was conducted on ion-implanted slices of PZO, LZO, and YTO single crystals, oriented down the [111] direction, using a Phillips CM300 FEG TEM, operating at an accelerating voltage of 297 kV. Off-center images were collected on an Orius CCD camera, while centered images were collected on film (Kodak SO 163). Patterns were collected under a large variety of exposure times (10–100 min) to determine the best exposure time to highlight the diffuse scattering, as demonstrated by Supplementary Figures 42, 43. Additional intensity scaling tricks, such as changing image brightness/contrast and inverting the colors, were used. A beam stop was not used both because the X-ray exposure times still remained in beam spilling, and to observe the completeness of the diffuse scattering.

**High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) imaging** was conducted on the PZO and LZO samples using a Nion UltraSTEM 100 with a C5 Nion QQ aberration corrector, operated at 100 kV at the Daresbury SuperSTEM Laboratory. The optics of the microscope were adjusted to form a 0.09 nm probe with 60 pA current. The beam convergence semi-angle was 30 mrad, while the detector angular range was calibrated at 85°. Imaging through (non-)rigid registration techniques$^{60}$, series of up to one hundred images were collected over a duration of several seconds. Subsequently, each image was realigned by an autocorrelation algorithm (and visual inspection for completeness) to remove time dependent drift before summing the series to form the final image. No filtering was performed on the images. Alternatively, the non-rigid registration algorithm SmartAlign was applied to some of the images to provide the highest precision possible.$^{61}$ The automatic peak finding algorithm Ranger$^{33}$ was used to extract experimental atomic positions from the STEM data, which uses 2-D Gaussian fit to obtain sub-pixel precision on the location of each column.

**EELS.** EELS was carried out using a Gatan Enfina spectrometer, with a collection semi-angle of 5 mrad. Spectrum images were acquired by rastering the probe serially across a pre-defined area of the sample and collecting both HAADF and EELS signals at each point. Compositional maps were extracted from these datasets by integrating the relevant intensity above the Zr and Pr $M_4,5$ EELS edge onset over a 50 eV energy window, after subtraction of the continuously decaying background using a power law model. Prior to integration, the signal was denoised using principal component analysis$^{62}$, taking great care that no artifact was introduced by this process through thorough inspection of the residuals. To remove the effects of multiple scattering, the signal was also deconvoluted using the Fourier-ratio method$^{62}$ using a low-loss spectrum image acquired immediately after the core loss datasets - the remarkably low drift and high stability of the instrument making this practical. Finally, the signal intensity for both elements was normalized to unity,– which the color map cannot be interpreted in terms of absolute composition, but nevertheless provide a useful indication on the relative distribution of the chemical elements across the field of view. Numerous chemical maps were acquired, systematically displaying close composition in atomic columns based on the elemental signal. The sample thickness varied from area to area, ranging between 0.45 and 0.70 inelastic mean free paths in the material (which is estimated...
to be 67 nm for PZO at 100 kV acceleration voltage. Though the EELS profiles shown in Supplementary Figure 46a follow the expected intensity patterns, the shape of the curves are odd, and several clear pixel outliers are seen in Supplementary Figures 46a, b which, in addition to previous comments, exemplify that this analysis is more qualitative than quantitative. Supplementary Figure 47 shows a same map used in the main text, along with the individual Pr and Zr maps, all processed in the same way.

To further quantify the amount of site mixing in the PZO sample, we analyzed line profiles of a HAADF STEM [110] image, which contains rows of mixed atomic columns and rows with alternating Pr/Zr atomic columns. Given that powder diffraction and PDF refinements indicate no site-mixing or off-stoichiometry, we assume that site mixing is a negligible contribution in rows with mixed cations columns; instead, effects such as varied sample thickness, sample bending, and multiple scattering dominate intensity fluctuations for mixed rows. Hence, the standard deviation of a mixed rows accounts for only experimental deviations of intensity.

Under this assumption, the errors for each atom type on alternating rows should be the same or less than that for mixed rows if no site-mixing or off-stoichiometry present.

To obtain the intensity maximum for each column a Gaussian was fit to each peak using DigitalMicrograph, and profiles were lined up for better comparison. The average intensity for mixed columns was 22.4(2) $10^6$ a.u. (taken over 60 atomic columns), was 21.92(19) $10^6$ a.u. for Zr columns (taken over 30 atomic columns), and 22.7(2) $10^6$ a.u. for Pr columns (taken over 30 atomic columns). The magnitude of the standard deviation, a 1% deviation from the average intensity for all column types, indicates that each contain similar errors, suggesting merely experimental effects rather than defect chemistry. Given that two standard deviations account for the intensity fluctuation of the mixed column rows, we use two standard deviations as the metric of experimental error for individual rows. Only one atomic column (third Zr column in row 2, shown in Supplementary Figure 48b) is observed to deviate beyond two standard deviations, indicating that the defect concentration is well below the 0.5% limit proposed by McQueen et al. 2017.

The authors declare that the data supporting the conclusions of this study are available within the article and its Supplementary Information file or from the corresponding author upon request. The Crystallographic data (Supplementary Data 1, 2) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC-1520136-1520137).

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References
1. Subramanian, M. A., Aravamudan, G. & Subba Rao, G. V. Oxide pyrochlores – a review. Prog. Solid State Chem. 15, 55–143 (1983).
2. Greedan, J. E. Frustrated rare earth magnetism: spin glasses, spin liquids and spin ices in pyrochlore oxides. J. Alloy. Compd. 408–412, 444–455 (2006).
3. Ramirez, A. P. Strongly geometrically frustrated magnets. Annu. Rev. Mater. Sci. 24, 453–480 (1994).
4. McQueen, T. M. et al. Frustrated ferroelectricity in niobate pyrochlores. J. Phys. Condens. Matter 20, 235210 (2008).
5. Tabira, Y., Withers, R. L., Minervini, L. & Grimes, R. W. Systematic structural change in selected rare earth oxide pyrochlores as determined by wide-angle XRD and a comparison with the results of atomistic computer simulation. J. Solid State Chem. 153, 16–25 (2000).
6. Wilde, P. J. & Catlow, C. R. A. Defects and diffusion in pyrochlore structured oxides. Solid State Ion. 112, 173–183 (1998).
7. Moriga, T. et al. Crystal structure analyses of the pyrochlore and fluoride-type Zr2CdO4 and anti-phase domain structure. Solid State Ion. 31, 319–328 (1989).
8. Clancy, J. P. et al. X-ray scattering study of pyrochlore iridates: crystal structure, electronic and magnetic excitations. Phys. Rev. B 94, 24408 (2016).
9. Shambil, J. et al. Probing disorder in isometric pyrochlore and related complex oxides. Nat. Mater. 15, 507–516 (2016).
10. Shoemaker, D. P., Llobet, A., Tachibana, M. & Seshadri, R. Reverse Monte Carlo neutron scattering study of the ‘ordered-ice’ oxide pyrochlore Pb5Ru4O12. J. Phys. Condens. Matter 23, 315404 (2011).
11. Thysgen, P. M. M. et al. Orbital dimer model for the spin-glass state in Y2Mo2O7. Phys. Rev. Lett. 118, 67201 (2017).
12. Spath, C. et al. Local lattice disorder in the geometrically frustrated spin-glass pyrochlore Y4Mn2O7. Phys. Rev. B 62, R755–R758 (2000).
13. Anderson, P. W. Ordering and antiferromagnetism in ferrites. Phys. Rev. 102, 1008–1013 (1956).
14. Bernal, J. D. & Fowler, R. H. A theory of water and ionic solution, with particular reference to hydrogen and hydroxyl ions. J. Chem. Phys. 1, 515–548 (1933).
15. Goodenough, J. B., Iversen, B. & Nguyen, H. B. Real-space refinement of single-crystal electron diffus scattering and its application to Bi6Ru4O10, J. Phys. Condens. Matter 19, 353216 (2007).
16. Shoemaker, D. P. et al. Atomic displacements in the ice pyrochlore Bi2Ti2O7 studied by neutron total scattering. Phys. Rev. B–Condens. Matter Mater. Phys. 81, 1–9 (2010).
17. Shoemaker, D. P., Seshadri, R., Tachibana, M. & Hector, A. L. Incoherent Bi off-centering in Bi2Ti2O7. Phys. Rev. B 84, 64117 (2011).
18. Fennie, C. J., Seshadri, R. & Rabe, K. M. Lattice instabilities in cubic pyrochlore Bi2Ti2O7, Preprint at https://arxiv.org/abs/0712.1846 (2007).
19. Esquivel-Elizondo, J. R., Hinojosa, B. B. & Nino, J. C. Bi2Ti2O7: it is not what you think it is. Phys. Rev. B 83, 144402 (2011).
20. Koohpayeh, S. M., Wen, J.-J., Trump, B. A., Broholm, C. L. & McQueen, T. M. Impact of stoichiometry of Yb2Ti2O7 on its physical properties. Phys. Rev. B 82, 035127 (2010).
21. Spin ice Pr2Zr2O7 pyrochlore. J. Phys. Condens. Matter 216, 94431 (2004).
22. McQueen, T. M. et al. Frustrated ferroelectricity in niobate pyrochlores. J. Phys. Condens. Matter 20, 235210 (2008).
23. Tabira, Y., Withers, R., Thompson, J. & Schmid, S. Structured diffuse scattering as an indicator of inherent cristobalite-like displacive phase transition in cristobalite, SiO2. Phys. Chem. Miner. 17, 554–562 (1991).
24. Seshadri, R. Lone pairs in insulating pyrochlores: ice rules and high-k behavior. Solid State Sci. 8, 259–266 (2006).
25. Tabira, Y., Withers, R., Thompson, J. & Schmid, S. Structured diffuse scattering as an indicator of inherent cristobalite-like displacive flexibility in the rare earth zirconate pyrochlore La3Zr2O7, 0.49-δ<5,0.51. J. Solid State Chem. 142, 393–399 (1999).
26. Koohpayeh, S. M., Wen, J.-J., Trump, B. A., Broholm, C. L. & McQueen, T. M. Synthesis, floating zone crystal growth and characterization of the quantum spin ice Pr2Zr2O7 pyrochlore. J. Cryst. Growth 402, 291–298 (2014).
27. Arpin, K. E., Trump, R. A., Scheie, A. O., McQueen, T. M. & Koohpayeh, S. M. Impact of stoichiometry of Yb2Ti2O7 on its physical properties. Phys. Rev. B 85, 94407 (2017).
28. Greedan, J. E. et al. Local and average structures of the spin-glass pyrochlore Y2Mo2O7 from neutron diffraction and neutron pair distribution function analysis. Phys. Rev. B–Condens. Matter Mater. Phys. 79, 1–10 (2009).
29. Williams, D. R. & Carter, B. C. Transmission Electron Microscopy (Spring Science, New York, NY, 2009).
30. Withers, R. L., Thompson, J. G. & Wellberry, T. R. The structure and microstructure of a-cristobalite and its relationship to b-cristobalite. Phys. Chem. Miner. 16, 517–523 (1989).
31. Tabira, Y., Withers, R. L., Yamada, T. & Ihashiwa, N. Annular dynamical disorder of the rare earth ions in a La4Zr2O7 pyrochlore via single crystal synchrotron X-ray diffraction. J. ferr. Krist. 216, 92–98 (2001).
32. Ofer, O., Keren, A., Gardner, J. S., Ren, Y. & MacFarlane, W. A. Origin of magnetic freezing in pyrochlore Y2Mo2O7. Phys. Rev. B–Condens. Matter Mater. Phys. 82, 4–7 (2010).
33. Sh𬞟, B. D. et al. Contribution of thermally scattered electrons to atomic resolution elemental maps. Phys. Rev. B–Condens. Matter Mater. Phys. 86, 1–9 (2012).
34. Shffield, B. D. & al. Local observation of the site occupancy of Mn in a MnFePSi compound. Phys. Rev. Lett. 114, 1–5 (2015).
35. Shffield, B. D. et al. Atomic structure study of the pyrochlore Yb2Ti2O7 and its relationship with low-temperature magnetic order. Phys. Rev. B 95, 94431 (2017).
33. Jones, L. & Nellist, P. D. Identifying and correcting scan noise and drift in the scanning transmission electron microscope. *Microsc. Microanal.* 19, 1250–1260 (2013).
34. Spurgeon, S. R. et al. Polarization screening-induced magnetic phase gradients at complex oxide interfaces. *Nat. Commun.* 6, 6735 (2015).
35. Pearson, R. G. Concerning jahn-teller effects. *Proc. Natl Acad. Sci.* USA 72, 2104–2106 (1975).
36. Baroudi, K., Gaulin, B. D., Lapidus, S. H., Gaudet, J. & Cava, R. J. Symmetry and light stuffing of H$_2$Ti$_3$O$_7$, Er$_3$Ti$_5$O$_{17}$, and Y$_2$Ti$_3$O$_7$ characterized by synchrotron X-ray diffraction. *Phys. Rev. B* 92, 24110 (2015).
37. Tabira, Y., Withers, R. L., Barry, J. C. & Elcoro, L. The strain-driven pyrochlore to 'defect fluorite' phase transition in rare earth sesquisoxide stabilized cubic zirconias, *J. Solid State Chem.* 159, 121–129 (2001).
38. Baroudi, K., Gaulin, B. D., Lapidus, S. H., Gaudet, J. & Cava, R. J. Symmetry and light stuffing of H$_2$Ti$_3$O$_7$, Er$_3$Ti$_5$O$_{17}$, and Y$_2$Ti$_3$O$_7$ characterized by synchrotron X-ray diffraction. *Phys. Rev. B* 92, 24110 (2015).
39. Popov, V. V. et al. Short- and long-range order balance in nanocrystalline Gd$_2$Zr$_2$O$_7$ powders with a fluoride-pyrochlore structure. *Russ. J. Inorg. Chem.* 59, 279–285 (2014).
40. Ma, E. Y. et al. Mobile metallic domain walls in an all-in-all-out magnetic insulator. *Science* 350, 538–541 (2015).
41. van Duijn, J. et al. Induced quadrupolar singlet ground state of prasodymium in a modulated pyrochlore. *Phys. Rev. B* 96, 094409 (2017).
42. Blanchard, P. E. R. et al. Investigating the local structure of lanthanide hafnates Ln$_2$Hf$_2$O$_7$ via diffraction and spectroscopy. *J. Phys. Chem. C* 117, 2266–2273 (2013).
43. Wen, J.-J. et al. A disordered route to the coulomb quantum spin liquid: random transverse fields on spin ice in Pr$_2$Zr$_2$O$_7$. *Phys. Rev. Lett.* 118, 107206 (2016).
44. Martin, N. et al. Disorder and quantum spin ice. *Phys. Rev. X* 7, 011028 (2017).
45. Ross, K. A. et al. Lightly stuffed pyrochlore structure of single-crystalline Yb$_2$Ti$_2$O$_7$ grown by the optical floating zone technique. *Phys. Rev. B: Condens. Matter Mater. Phys.* 86, 174424 (2012).
46. Donnerer, C. et al. All-in-all-out magnetic order and propagating spin waves in Sm$_3$Ir$_2$O$_7$. *Phys. Rev. Lett.* 117, 37201 (2016).
47. Cook, W.R., & Jaffe, H. Ferroelectricity in oxides of face-centred cubic lattice. *Acta Crystallogr. Sect. A* 50, 439–445 (2003).
48. Chaikovskos, B. C. Systematics of the pyrochlore structure type, ideal A$_2$B$_2$X$_6$. *J. Solid State Chem.* 53, 120–129 (1984).
49. Cai, L., Arias, A. L. & Nino, J. C. The tolerance factors of the pyrochlore crystal structure. *J. Mater. Chem. C* 21, 3611 (2011).
50. Brik, M. G. & Sviratava, A. M. Pyrochlore structural chemistry; predicting the lattice constant by the ionic radii and electronegativities of the constituting ions. *J. Am. Ceram. Soc.* 95, 1454–1460 (2012).
51. Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* 32, 751–767 (1976).
52. Koohpayeh, S. M., Fort, D. & Abell, J. S. The optical floating zone technique: a review of experimental procedures with special reference to oxides. *Prog. Cryst. Growth Charact. Mater.* 54, 121–137 (2008).
53. Toby, B. H. & Von Dreele, R. B. GSAS-II: the genesis of a modern open-source all purpose crystallography software package. *J. Appl. Crystallogr.* 46, 544–549 (2013).
54. Momma, K., & Izumi, F. VESTA: a three-dimensional visualization system for electronic and structural analysis. *J. Appl. Crystallogr.* 41, 653–658 (2008).
55. Hammersley, A. P., Svensson, S. O., Hand, M., Fitch, A. N. & Hausermann, D. Two-dimensional detector software: from real detector to idealised image or two-theta scan. *High Press. Res.* 14, 235–248 (1996).
56. Qiu, X., Thompson, J. W. & Billinge, S. J. L. PDFgetX2: a GUI-driven program to obtain the pair distribution function from X-ray powder diffraction data. *J. Appl. Crystallogr.* 37, 678 (2004).
57. Neuefeind, J., Feygenson, M., Carruth, J., Hoffmann, R. & Chipley, K. K. The nanoscale ordered materials diffractometer NOMAD at the spallation neutron source SNS, *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* 287, 68–75 (2012).
58. Farrow, C. L. et al. PDRefit2 and PDFgui: computer program for studying nanostructure in crystals. *J. Phys. Condens. Matter* 19, 335219 (2007).
59. Jones, L. Quantitative ADF STEM: acquisition, analysis and interpretation. *JOP Conf. Ser. Mater. Sci. Eng.* 109, 12008 (2016).
60. Jones, L. et al. Smart align – a new tool for robust non-rigid registration of scanning microscope data. *Adv. Struct. Chem. Imaging* 1, 8 (2015).
61. Watanabe, M., Okunishi, E. & Ishizuka, K. Analysis of spectrum-imaging datasets in atomic-resolution electron microscopy. *Microsc. Anal.* 23, 5–7 (2009).
62. Egerton, R. Electron Energy Loss Spectroscopy in the Electron Microscope (Springer, Berlin, 2011).

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Author contributions

All authors have given approval to the final version of the manuscript. S.M.K., J.-J.W., K. E.A., and B.A.T. prepared samples and collected diffraction data. M.F. helped conduct neutron PDF acquisition. K.J.T.L., Q.M.R. and R.B. were involved with HR-STEM measurements with analysis conducted by K.J.T.L., Q.M.R., and B.A.T., H.T., M.T., K.K., and S.N. conducted and analyzed NQR data. C.L.B. and T.M.M. initiated and oversaw the project. B.A.T. did structural refinements and wrote the manuscript with input from all authors.

Additional information

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