Average and Local Structure of Apatite-Type Germanates and Implications for Oxide Ion Conductivity

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ABSTRACT: Materials with the apatite structure have a range of important applications in which their function is influenced by details of their local structure. Here we describe an average and local structural study to probe the origins of high temperature oxide ion mobility in La_{10}(GeO_{4})_{6}O_{3} and La_{8}Bi_{2}(GeO_{4})_{6}O_{3} oxygen-excess materials, using the low-conductivity interstitial oxide-free La_{8}Sr_{2}(GeO_{4})_{6}O_{2} as a benchmark. For R = La and Bi we locate the interstitial oxygen, O_{int}, responsible for conductivity by Rietveld refinement and relate the P6_{3}/m to P1 phase transitions these phases undergo on cooling to oxygen ordering. Local structural studies using neutron total scattering reveal that well-ordered GeO_{5} square pyramidal groups form in the structure at low temperature, but that O_{int} become significantly more disordered in the high-conductivity high-temperature structures, with a transition to more trigonal-bipyramid-like average geometry. We relate the higher conductivity for R = Bi to the presence of several O_{int} sites of similar energy in the structure, which correlates with its less-distorted low temperature average structure.

Introduction

Apatites are materials with the general formula A_{10}(MO_{4})_{6}X_{2±}, where A = alkaline or rare earth metal, M = Ge, Si or P and X = halides, O^{2−} or [OH] −. Compounds adopting this structure type are ubiquitous both as natural bio-materials and as synthetic functional materials with a range of technological applications. They are therefore of significant research interest in areas as diverse as materials chemistry, physics, engineering, medicine, archaeology and conservation science.

In all its roles, the fine details of the apatite structure, and in particular short-range local structure, have a critical impact on its physical or structural properties. For example, symmetry-lowering deviations from the ideal apatite structure and differing arrangements of ions in its channels are important to the function of natural bone and tooth enamel (carbonated calcium phosphate hydroxyapatite), and the use of apatite-type synthetic materials in bone grafts and implants.1-5 In particular, the details of the local coordination environment of Ca^{2+} ions are necessary for understanding bone formation and diseases, but this information is hard to obtain given the experimental difficulty of techniques such as ^{45}Ca solid state NMR.6-8 Similar research questions regarding apatite-type materials are important in archaeological science and anthropology.9-12

In the context of modern technological applications, departures from the ideal centrosymmetric crystal structures make some apatite-type materials second harmonic generation (SHG) active and potentially suitable for non-linear optical (NLO) applications.13-14 Apatite-type oxides are also promising hosts for the development of phosphors for solid-state lighting. In this application, the local environment and symmetry of the crystallographic sites occupied by the dopant activator ions significantly influence luminescence probabilities and energy transfer processes, and hence the emission properties of the phosphors.15-18 Certain apatite-type lanthanum germanates and silicates also exhibit high oxide ion conductivities, making them applicable in oxygen sensors and pumps,19 separation membranes,20-21 and solid oxide fuel cells (SOFCs).22-24 These applications are the focus of this paper.

The ideal apatite structure (x = 0 in A_{10}(MO_{4})_{6}X_{2±}) can be described as a framework in which columns of face-sharing AO_{6} trigonal prisms share corners with TO_{4} tetrahedra (dark green and grey polyhedra, respectively, in Figure 1a) to form channels running down the crystallographic c-axis; these channels are filled by A_{6}X_{2} constituents (represented by light green and pink spheres in Figure 1a). The space group is usually hexagonal P6_{3}/m, although lower-symmetry variants are also known.25 The AO_{6} trigonal prism twist angle ϕ has been used as a quantitative parameter indicative of the geometry of the framework and symmetry of the material.26 If the size of the channels is large relative to the units occupying it, the A cations in the channels tend to be under-bonded and the tetragonal T cations over-bonded; to remove this unfavourable situation, the framework trigonal prisms twist. A recent density functional theory (DFT) computational study 27 of a series of hexagonal and trigonal apatites with A cations of very similar sizes, A_{10}(PO_{4})_{6}F_{2} (A=Ca, Sr, Pb, Cd, Hg), found the symmetry lowering to be an electronic effect associated with mixing of the occupied (n−1)d and the empty ns states for A = Cd and Hg. In these cases the authors propose a particular displacive mode, associated with cooperative tilts of the TO_{4} tetrahedra belonging to the Γ_{s}Γ_{s} irreducible representation (irrep), as driving the P6_{3}/m to P1 phase transition.

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Figure 1. (a) The hexagonal $P6_3/m$apatite structure, exemplified by the high-temperature average structure of La$_{10}$(GeO$_4$)$_6$O$_3$ viewed down the $c$-axis; (b) Labels of different potential O$_{int}$ sites (orange spheres, A–F) in the $P1$ apatite structure. The grey tetrahedra show GeO$_4$ groups and are included to highlight their proximity to the O$_{int}$. Symmetry-unique GeO$_4$ tetrahedra are numbered.

Oxygen-excess ($x = 1$) La$_{10}$(GeO$_4$)$_6$O$_3$ and La$_8$Bi$_2$(GeO$_4$)$_6$O$_3$ are both excellent oxide ion conductors, with $\sigma \approx 7.8 \times 10^{-3}$ and $1.3 \times 10^{-2}$ S/cm at 775 °C, respectively. The room temperature structure of La$_{10}$(GeO$_4$)$_6$O$_3$ has been described as triclinic from low-resolution powder neutron diffraction data, while the high temperature structure has not been reported. The structure of La$_8$Bi$_2$(GeO$_4$)$_6$O$_3$ has been studied by high-resolution synchrotron X-ray and neutron diffraction data and found to be triclinic at room temperature and hexagonal at 800 °C. There is a general consensus in the literature, both from diffraction-based investigations of the average structure and from computational studies, that the most likely location for the extra oxygen (O$_{int}$) atoms in apatite-type germanates is between the opposite faces of adjacent GeO$_4$ tetrahedra (locations represented by orange spheres in Figure 1). In space group $P6_3/m$, these locations correspond to a single unique crystallographic site (Wyckoff site 6g). When the symmetry is lowered to triclinic $P1$, however, they become 6 independent crystallographic sites. The potential locations of interstitial O$_{int}$ sites in the unit cell are shown in Figure 1b and labelled A–F. Pramana et al. located the O$_{int}$ atoms on the B-sites of La$_{10}$(GeO$_4$)$_6$O$_3$, while Tate et al. found the O$_{int}$ atoms to be distributed over several site of La$_8$Bi$_2$(GeO$_4$)$_6$O$_3$. The experimental limitations in these works were the reliance on difference Fourier maps generated from relatively low-resolution powder neutron diffraction data in the former case, and the use of the HAADF-STEM method which is an inherently two-dimensional probe, in the latter.

The aim of this work was to experimentally probe the local structure of two apatite-type oxide ion conductors, La$_{10}$(GeO$_4$)$_6$O$_3$ and La$_8$Bi$_2$(GeO$_4$)$_6$O$_3$, as a function of temperature and correlate the local structure with the measured properties and with density functional theory (DFT) simulations of their oxide ion conductivity. In addition to these triclinic examples, we also studied hexagonal La$_8$Sr$_2$(GeO$_4$)$_6$O$_2$ ($x = 0$, no interstitial oxygen) to provide a reference point for the interpretation of structure-property relationships in the two triclinic oxygen-excess materials. We used variable temperature neutron total scattering and Reverse Monte Carlo (RMC) modeling to derive local structural models which account for the higher conductivity found for La$_8$Bi$_2$(GeO$_4$)$_6$O$_3$.

**Experimental**

**Synthesis**

Two 5 g samples of La$_8$R$_2$(GeO$_4$)$_6$O$_2+ x$ for each of R = Sr, La and Bi were prepared by hand-grinding stoichiometric amounts of La$_2$O$_3$ (Acros, 99.9%, heated at 950 °C for 12 h prior to synthesis), SrCO$_3$ (Fisher, 99.9%), Bi$_2$O$_3$ (Fisher, 99.9%) and GeO$_2$ (Acros, 99.999%). The samples were heated at 1100 °C for 16–36 h followed by a further heating at 1300 °C and 1100 °C for R = Sr, La and R = Bi respectively, with intermittent grinding. The two 5 g batches were mixed and then heated at 1300, 1200 and 1100 °C for R = Sr, La and Bi respectively. All products were pale cream in colour. Samples were also heated at 1000 °C for 12 h immediately prior to neutron/synchrotron powder diffraction studies on HRPD and I11. For La$_8$Bi$_2$(GeO$_4$)$_6$O$_3$ this treatment appeared to give rise to small impurity phases, and a fresh 5 g sample was prepared for later neutron total scattering data collections on POLARIS. All heating and cooling rates were set to 10 °C min$^{-1}$. Phase purity was assessed using laboratory X-ray powder diffraction data collected on a D8 Bruker Advance with Cu Kα$_{1/2}$ radiation, a Ni filter and Lynxeye detector. Samples were mounted on Si zero-background slides and typically scanned over a $10^\circ \leq 2\theta \leq 80^\circ$ range in 0.02° steps for 1 second per step.

**Synchrotron Powder Diffraction**

Synchrotron X-ray powder diffraction data were collected using a wavelength of $\lambda = 0.8259211$ Å, determined from a Si standard, on samples loaded into 0.3 mm diameter fused silica capillaries at the Diamond Light Source beamline I11. A hot air blower was used to control the temperature for variable temperature data collections. The samples were heated from
30–800 °C in 25 °C steps with a scan time of 1 hour at 30 °C and 800 °C and 5 minutes for the intervening scans. The temperature was calibrated with an Al2O3 standard. Room temperature experiments on La8Sr2(GeO4)6O2 to investigate unusual peak shapes used 30 minute data collections with λ = 0.824681 Å.

Neutron Scattering

High resolution neutron powder diffraction data were collected for La8R2(GeO4)6O2 in 11 mm vanadium cans (sample heights of ~2.5 cm and masses of ~3.0 g) on the High Resolution Powder Diffraction (HRPD) instrument at the ISIS Neutron and Muon Source. A 6 hour scan was collected at room temperature for all samples. For La8(GeO4)6O2, 6 minute measurements were recorded from 100–840 °C in 20 °C increments to follow cell parameter evolution, followed by six 1 hour measurements at 850 °C. Equivalent data were recorded for La8Bi2(GeO4)6O2 but with a maximum temperature of 800 °C. For La8Sr2(GeO4)6O2, 6 minute measurements were recorded from 90–850 °C. Data of suitable quality for PDF analysis were recorded using the ISIS POLARIS diffractometer on ~2.7 g samples of La8R2(GeO4)6O2, in 8 (R = La, Sr) or 6 (R = Bi) mm vanadium cans with sample heights of ~4.7 cm. 6 × 1 h measurements were recorded for each sample at room temperature. 6 × 1 h measurements were performed at 850 °C for R = La and 800 °C for R = Bi.

Data were processed for Rietveld refinement using routines within Mantid software and an absorption correction applied. PDF data were processed using GudrunN3 version 5 to produce S(Q) data and the STOG33 software package was used to create G(r) and P(Q) files. G(r) data were produced using Qmax = 5 Å−1 and a Lorch function34 was applied to remove Fourier ripples due to the limited Qmax. Low-r data were Fourier-filtered as follows: R = Sr, r ≤ 1.6 Å (room temperature); R = La; r ≤ 1.52 Å (room temperature) and r ≤ 1.55 Å (850 °C); R = Bi: r ≤ 1.55 Å (room temperature) and r ≤ 1.57 Å (800 °C).

Rietveld Refinement

Rietveld refinements were performed using TOPAS v6.35–36 Average structural models were derived from starting models published by Pramana et al. (R = La,29 Sr37) and Tate et al. (R = Bi39). For combined refinements, HRPD banks 3 (2θ = 52.2461°) were used in the RMCProfile refinement. The G(r) data were fitted as G(r). 5 ×5×4 (~50×50×30 Å; a ≈ b ≈ 90°, γ ≈ 120°) supercells were generated from the Rietveld models containing a total of 4,200 sites for R = Sr. For R = La, Bi, an extra 600 or 1200 sites were used to describe interstitial oxygen (Oint) positions A – F (Figure 1b), and equivalent vacancy positions. Site swapping procedures were used during the RMCProfile modelling to test data sensitivity to different Oint distributions. Minimum distance restraints were applied to prevent unreasonably short atomic approaches, and weak bond valence restraints were applied to maintain chemically plausible structures. Convergence and a good fit to experimental data was typically achieved after approximately 5 ×106 moves (approximately 15 hours on a standard desktop PC). A minimum of 8 different configurations were used for each set of data fitted and the resulting configurations averaged during data analysis. "Cloud plot" figures were drawn using the VESTA software package.41

PDF Analysis

Total scattering analysis was performed using TOPAS v6.35–36 for small-box analysis by converting the G(r) data produced by STOG into D(r) normalised to the sum of the scattering of all atomic pairs according to standard formalisms.38 RMCProfile40 was used for big-box analysis. The G(r) and P(Q) produced by STOG and the Bragg scattering data from POLARIS bank 3 (2θ = 52.2461°) were used in the RMCProfile refinement. The G(r) data were fitted as D(r). 5 ×5×4 (~50×50×30 Å; a ≈ b ≈ 90°, γ ≈ 120°) supercells were generated from the Rietveld models containing a total of 4,200 sites for R = Sr. For R = La, Bi, an extra 600 or 1200 sites were used to describe interstitial oxygen (Oint) positions A – F (Figure 1b), and equivalent vacancy positions. Site swapping procedures were used during the RMCProfile modelling to test data sensitivity to different Oint distributions. Minimum distance restraints were applied to prevent unreasonably short atomic approaches, and weak bond valence restraints were applied to maintain chemically plausible structures. Convergence and a good fit to experimental data was typically achieved after approximately 5 ×106 moves (approximately 15 hours on a standard desktop PC). A minimum of 8 different configurations were used for each set of data fitted and the resulting configurations averaged during data analysis. "Cloud plot" figures were drawn using the VESTA software package.41

Results and Discussion

Average Structure and Phase Transitions

Powder diffraction showed that high purity samples of La8R2(GeO4)6O2 (R = Sr, La, Bi) could be prepared. In the large samples prepared for neutron scattering experiments, the R = Sr sample contained an ≲ 1 weight % Sr3GeO3 impurity, the R = La sample a ≲ 1 % La2GeO3 impurity and the R = Bi sample a ≲ 1 % La2Ge2O7 impurity. Rietveld plots of combined synchrotron X-ray and HRPD neutron refinements are given in the supplementary Figures S1 to S6 for room temperature (R = Sr, La, Bi) and 850/800 °C (R = La, Bi) data.

There has been some debate in the literature as to the true symmetry of the R = Sr (x = 0) phase; the presence of apparent peak splittings and broadening in the reported room temperature powder diffraction patterns prompted some authors to propose monoclinic symmetry at room temperature.26 We also observed unusual peak splittings in samples synthesised at 1300 °C, but found that they could be explained by assuming that a mixture of hexagonal phases with slightly different cell parameters was present, suggesting compositional inhomogeneity. The fits obtained to high-resolution synchrotron X-ray diffraction data using a multi-phase model in which cell parameters vary linearly with composition are shown in Figure S1. Heating to higher temperature (e.g. 1350 °C for 16 h) produced a phase with sharp peaks consistent with hexagonal P6/m symmetry, as shown by the fits in Figure S2. We therefore conclude this is the correct space group for room temperature R = Sr. Consistent with earlier studies, Rietveld refinement using both low- and high-temperature data suggested that Sr is located primarily (95%) on the A1 trigonal prismatic 4f site (dark green polyhedra in Figure 1).
Room temperature powder patterns for \( R = \text{La} \) and \( R = \text{Bi} \) are significantly more complex, in line with the \( P\bar{6}1 \) symmetry previously reported.\(^{29-30}\) Samples showed a significant \( hkl \)-dependence to their peak shape, which is consistent with the strain broadening expected from the symmetry-lowering phase transition (discussed below) that occurs as they are cooled from high temperature. Peak shapes could be described by convoluting a \( hkl \)-dependent spherical harmonic function describing strain broadening onto the instrumental and isotropic sample contributions to the peak shape. We note that this approach is not possible in the RMCProfile modelling discussed below. Bi was found to occupy solely the A2 site within uncertainty.

One of the aims of this study is to identify the positions of the additional oxygen in for \( R = \text{La} \) and \( R = \text{Bi} \) (\( x = 1 \) in \( \text{La}_x\text{R}_y(\text{GeO}_4)_6\text{O}_{2}+ \)) compared to \( \text{Sr} (x = 0) \); we call this 27th oxygen per formula unit \( \text{O}_{\text{int}} \). The distribution of the excess oxygen atoms over likely sites A–F (Figure 1b) was determined by combined Rietveld fitting of synchrotron X-ray and HRPD high resolution neutron powder data. After refining a model with no \( \text{O}_{\text{int}} \), oxygen were introduced on 2i Wyckoff sites close to positions A–F with occupancy 1/2 (giving one \( \text{O}_{\text{int}} \) per formula unit or \( x = 1 \)). Their occupancies were refined with a soft restraint applied to maintain the overall \( \text{O}_{\text{tot}} \) composition, a constrained minimum value of zero and a soft restraint was applied to keep them close to the midpoint of two tetrahedra (an inversion centre in \( P\bar{6}1 \)). Repeated cycles of full Rietveld refinement and randomisation of occupancies and coordinates consistently showed low or zero occupancy of sites D, E and F. Final \( \text{O}_{\text{int}} \) occupancies at sites near A/B/C were 0.08(1)/0.46(1)/0.06(1) for \( \text{A/B/C} \) sites. For \( R = \text{Bi} \), Polaris data were recorded on a physically different sample and gave A/B/C/D/E/F occupancies of 0.13(1)/0.21(1)/0.02(1)/0.01(1). These differences could reflect the difficulties in determining oxygen content by Rietveld refinement, as discussed below, or minor changes in oxygen distribution due to different sample thermal histories.

Even using neutrons, the contribution of the single \( \text{O}_{\text{int}} \) per unit cell to the total scattering is relatively small (2.5 %), such that the determination of \( \text{O}_{\text{int}} \) positions is challenging from powder diffraction data. It is also worth noting that the symmetry reduction from \( P6_3/m \) to \( P\bar{6}1 \) could give rise to six different domains in a single crystal based on the different basis vector choices relative to the parent structure. For a polycrystalline sample this means there are six equivalent cell parameter choices with similar but subtly different values. These are tabulated for \( R = \text{La} \) in supplementary Table S6. Choosing a different set of cell parameters in the triclinic fit is equivalent to selecting a different domain, and will change the labelling of the various \( \text{O}_{\text{int}} \) sites (ESI Table S6). Care must therefore be taken when comparing different refined models. Despite these caveats, our data suggest the B site has significant occupancy in both the La and Bi phase, with some density on site A. Ge sites Ge2 and Ge3, which lie on the BD and AC \( \text{O}_{\text{int}} \) chains respectively, show the most significant departure from tetrahedral bond angles, consistent with this occupation pattern. In contrast, tetrahedral bond angles in Ge1, which lie along the EF chains, remain relatively undistorted with standard deviations of the 6 tetrahedral angles similar to those in the hexagonal \( R = \text{Sr} \) case. Average Ge1O4 bond angles and standard deviations of 109.4±4.6; 109.2±5.4 and 109.6±3.7° were obtained for \( R = \text{La} \), Bi and Sr respectively. Values for all tetrahedra are given with other important structural parameters for the three phases in Table 1.
Figure 2. Unit cell edges and angles derived from variable temperature synchrotron powder diffraction studies of La₆R₂(GeO₄)₆O₂₊ₓ. (a) R = Sr; (b) volume of all phases; (c)–(d) R = La; (e)–(f) R = Bi. For R = La, Bi a triclinic model was used at all temperatures. Note that γ (≈ 120°) is plotted on the right hand scale of (d) and (f) to emphasise the cell angle-convergence at the phase transition to P₆₃/m.

Figure 2 shows the unit cell parameter evolution for each sample between room temperature and ~850 °C extracted by Rietveld refinement using synchrotron X-ray data. Values obtained from high resolution neutron powder diffraction experiments are essentially identical and are shown in ESI Figure S7. Each material shows positive thermal expansion with α₉₉ = 26.5(2), 29.1(6) and 29.0(5) × 10⁻⁶ K⁻¹ between 100 °C and 700 °C for R = Sr, La and Bi respectively. For R = La and Bi we see a clear indication of a phase transition to hexagonal symmetry at T = 780 and 740 °C with a and b cell edges converging, angles α/β approaching 90° and angle γ approaching 120°. Whilst a symmetry analysis using ISODISTORT shows that a P₆₃/m to P1 transformation could occur via a number of intermediate subgroups (e.g. P3, P2₁/m), it can be described using a single Γ₄₊Γ₆ irrep describing O₉₉ ordering, and is allowed to be continuous by Landau theory. We see no evidence in the diffraction data for simple intermediate phases, which would all require at least one 90° cell angle. We do see a subtle change in thermal expansion for R = Bi in the X-ray and neutron data around 250 °C, which could suggest the onset of partial O mobility. One notable feature in Figure 2 and Table 1 is the smaller metric distortion from hexagonal for R = Bi than R = La, manifested in the smaller differences between the unit cell parameters a and b, and the smaller deviations of the unit cell angles from 90 and 120° for R = Bi; we return to this point below.

As discussed in the Introduction, previous workers have described the P₆₃/m to P1 phase transition in Cd and Hg fluorophosphate O₉₉-free apatites in terms of a soft mode Γ₄₊Γ₆ irrep distortion which causes a cooperative tilting of tetrahedra when frozen into the structure. Instead of using conventional crystallographic fractional coordinates, we can describe our room temperature structures of the P1-La phase in terms of the high temperature P₆₃/m parent structure plus the amplitude of 63 symmetry-adapted-distortion-modes using the language of Campbell, Stokes and co-workers. We find that 16 of the 63 allowed modes have irrep Γ₄₊Γ₆. These Γ₄₊Γ₆ modes appear to dominate the structural distortion, with 6 of the 9 largest amplitude modes belonging to this irrep. These modes alone describe the essence of the GeO₄ displacements and distortions. We see similar behaviour for R = Bi, and histograms of mode amplitudes are included for both phases in ESI Figure S8. Comparing mode amplitudes between R = La and R = Bi we see, as expected, that the two structures display very similar distortions. On average, mode amplitudes (which give the root-summed-squared displacement of atoms in the child cell) for R = Bi are around 2/3 of their values for R = La, another representation of its lower distortion. The most significant difference between the two structures is in the O₄ (O’) z-coordinate. O₄ is coordinated exclusively by A2 cations and its position could be influenced by the lone pair cations on these sites, as indicated in previous theoretical studies.43
Local Structure

Further insight into the coordination environments of O\textsubscript{int}, their influence on the surrounding coordination polyhedra and the implication of their temperature evolution on conductivity requires a local rather than average structural probe. We have used big-box modelling using 5×5×4 supercells within the RCMProfile package to simultaneously fit Bragg, D(r) and F(q) data from each sample. For R = Sr excellent agreement with experimental data was obtained from each of 8 different RMCProfile starting configurations. Representative fits to Bragg and PDF data are shown in Figure 3a/b (F(Q) fits shown in ESI Figure S9). As expected for an ordered structure, the “cloud plots” of atomic density produced by folding the supercell configurations back into a single unit cell show good agreement with the average structural model (Figure 4a) and with the size of the atomic displacement parameters. Bond lengths and bond angle distributions around GeO\textsubscript{4} were as expected for regular tetrahedra. Fitting the observed distributions (ESI Figure S10a/b) in all 8 configurations to Gaussian functions gave a mean Ge–O bond length of 1.7584(7) Å and O–Ge–O angles of 108.91(3)°; the full width at half maximum (fwhm) of the distributions were 0.176(1) Å and 20.33(7)° respectively. The corresponding bond length determined from Rietveld refinement was 1.741(8) Å and angles ranged from 103.9 to 114.9°. The difference between the Rietveld- and RMCProfile-derived bond lengths is presumably caused by the well-known shortening of refined bond lengths when harmonic displacement parameters are used for groups undergoing correlated motion.44
For \( R = \text{La} \) and Bi, four models were tested to describe the \( O_{\text{int}} \) distribution and how it influences conclusions about local structure. These involved starting \( O_{\text{int}} \) atoms on sites to mimic the distribution indicated by Rietveld refinement, or statistically placing them across all available sites. During RMCProfile modelling \( O_{\text{int}} \) was then either limited to swapping between just the Rietveld sites or allowed to visit all sites A–F. After convergence we find that the \( O_{\text{int}} \) distribution broadly follows that derived by Rietveld refinement (ESI Table S 7). This occurs despite RMC methods favouring random models and is caused, at least in part, by the GeO\(_4\) distortions present in the Rietveld-derived average model, meaning that certain \( O_{\text{int}} \) sites provide more favourable local environments in terms of an absence of short contacts with neighbouring oxygens. Importantly, analysis of different models showed that the local structural information derived and discussed below was independent of the \( O_{\text{int}} \) model used. The results are therefore based on the average of 8 starting configurations in which \( O_{\text{int}} \) was allowed to populate all possible sites starting from a statistically-distributed configuration.

Figure 3 shows typical fits to the room temperature Bragg and \( D(r) \) data for \( R = \text{La} \) (Figure 3c, 3d) and \( R = \text{Bi} \) (Figure 3e, 3f); Figure 5 shows equivalent fits above the \( P\bar{1} \) to \( P\bar{6}_3/m \) transition. \( F(Q) \) plots are included in ESI Figure S9. We see good agreement between observed and calculated data in all cases. The largest discrepancies are the reflections for \( R = \text{La} \) at \( -13500 \) \( \mu \)s (\( d \approx 4 \) \( \AA \)) which derive from the parent (2, –1, 1): whilst the overall intensity of this reflection is captured correctly, we are not able to describe the \( hkl \)-dependent peak shape during RMCProfile modelling. We note that this peak is fitted much better in the Rietveld plot of Figure S3d.

Figure 4. Cloud plots showing volumes enclosing oxygen sites in (a) \( \text{La}8\text{Sr}(\text{GeO}_4)_6\text{O}_2 \) and (b-d) \( \text{La}_{10}(\text{GeO}_4)_6\text{O}_3 \). (a) shows clouds for all atoms. (b) Shows only \( \text{GeO}_5 \) groups where \( O_{\text{int}} \) is part of Ge coordination sphere at room temperature. (c) Shows only \( \text{GeO}_5 \) groups at 800 °C. (d) Shows only \( \text{GeO}_4 \) groups at 800 °C. Yellow surface drawn at 2% of maximum grid value in each plot; contours blue to red where cloud surfaces interact the cell edges show the probability of population of different regions. The most important information from PDF modelling concerns the local coordination geometry around \( O_{\text{int}} \) and how it changes with temperature. By analysing each Ge site in the big-box configuration we can probe individual \( \text{GeO}_4 \) groups and how they vary depending on the location of \( O_{\text{int}} \). Histograms of bond distances and angles around Ge groups (ESI Figure S10) show that the \( \text{GeO}_4 \) polyhedra fall into two distinct categories: \( \text{GeO}_4 \) tetrahedra (84% of total) which are remote from \( O_{\text{int}} \) sites and \( \text{GeO}_5 \) polyhedra (16%) where \( O_{\text{int}} \) enters the coordination sphere. This is consistent with \( ^{17}\text{O} \) NMR studies on \( \text{La}_3\text{Y}_2\text{Ge}_6\text{O}_{27}.45 \) Whilst it would also be possible to produce \( \text{GeO}_6 \) groups if two nearby \( O_{\text{int}} \) sites were simultaneously occupied and close to the same Ge (e.g. B and D close to Ge2 in Figure 1b), the number of such groups is extremely small in our configurations. We can produce cloud plots showing the local geometries near \( O_{\text{int}} \) by folding all the \( \text{GeO}_3\text{O}_{\text{int}} \) groups from all configurations back into a single crystallographic cell as shown in Figures 4b and 4c for \( R = \text{La} \). Since the plots of Figure 4 use a single unit cell, they average the big-box configuration in a fashion similar to the average crystallographic model meaning that the "double clouds" or "peanut" \( O_{\text{int}} \) shapes represent sites that are not occupied simultaneously. We can see, however, that \( O_{\text{int}} \) sites are relatively localised at low temperature (Figure 4b) but become significantly more diffuse at high temperature (Figure 4c).
Figure 5. Representative RMCProfile fits of $La_8R_2(GeO_4)_6O_3$ at 850 °C (R = La) and 800 °C (R = Bi); (a) R = La Bragg; (b) R = La PDF; (c) R = Bi Bragg; (d) R = Bi PDF.

The cloud plots of Figure 4 help understand the origin of the high oxide ion conductivity in oxygen excess apatite-type germanates. Recent density functional theory (DFT) studies of the $La_{10-y}Bi_yGe_6O_{27}$ (y=0, 2, 4) series, supported by neutron scattering experiments, have calculated the oxide ion migration pathways in these materials and provided new insight into the lone pair effects associated with the presence of Bi(III). The ab initio simulations identified four oxide ion exchange mechanisms contributing to the ionic conductivity, with the main one based on oxide ion transport in the c-direction via the ...GeO₄ – GeO₅ – GeO₄... network. This mechanism, prevalent at all simulation temperatures for all compositions in the series, gives rise to ionic displacement clouds that are very similar in appearance to the atomic density map shown in Figure 4c.

Focussing on the geometries of individual GeO₄ polyhedra, we find that GeO₄ tetrahedra are only slightly more distorted than in the R = Sr case (fwhm of angle distribution 20.3°, 23.2° and 30.2° for R = Sr, La, Bi respectively), whereas the GeO₅ groups display a much broader distribution of bond angles with maxima at ~90, 140 and 160°. Bond angle histograms are given in ESI Figure S10. We can gain more insight into the geometry of the GeO₅ polyhedra from the histograms of Figures 6 and 7. Figure 6 shows a histogram of the difference-in-distance between O_int and its two neighboring Ge (i.e., the Ge–O·····Ge local asymmetry). For both R = La and R = Bi we observe a strong preference for each O_int to have one short and one long Ge–O distance at room temperature. This is consistent with local bond valence considerations. If we take a typical Ge–Ge separation of 4 Å, an O placed midway between the two would have a bond valence sum of ~1.0. Displacing O_int locally to give bond lengths of 1.6 and 2.4 (Δr = 0.8 Å as observed experimentally, Figure 6a) gives a more reasonable bond valence sum of ~1.7.

Figure 6. Histograms of ΔGe–O_int distances in (a) $La_8(GeO_4)_6O_3$ at room-temperature (purple line) and 850 °C (gold bars) and; (b) $La_8Bi_2(GeO_4)_6O_3$ at room-temperature (blue) and 800 °C (red). Distances Δr defined in inset to (b).
La_{10}(GeO_{4})_{6}O_{3} and La_{8}Bi_{2}(GeO_{4})_{6}O_{3} both adopt triclinic $\hat{P}$1 symmetry at room temperature and hexagonal $P6_{3}/m$ symmetry at high temperature, as previously reported. Rietveld refinement shows that the single O_{int} atom per formula unit lies between GeO_{4} tetrahedra. Multiple sites can be occupied: the B site is strongly-favoured in La_{10}(GeO_{4})_{6}O_{3} and the A, B and C sites are occupied in La_{8}Bi_{2}(GeO_{4})_{6}O_{3}. The preferential occupation of certain sites drives the phase transition to $\hat{P}$1. The less-complete site ordering for R = Bi presumably occurs due to the distribution of La and Bi atoms on the A2 site (2:1 on average, but there will be local deviations from this) leading to a range of energies for nearby O_{int} sites. Previous computational studies have also shown that the Bi lone pair gives rise to significant local structural distortions. Due to the similar neutron scattering lengths of La and Bi, our local studies can't probe this aspect of the structure. The wider O_{int} distribution for R = Bi is presumably the reason why it shows a smaller distortion from hexagonal symmetry at room temperature than R = La. The presence of similar-energy O_{int} sites can then explain the lower phase transition temperature to $P6_{3}/m$ and underpin the higher O_{int} conductivity of R = Bi. Less stable O_{int} sites may also redistribute at low temperature, leading to the small discontinuity in the cell parameters observed at around 250 °C.

Local structural analysis shows that the O_{int} atoms are predominantly present in GeO_{4} square planar units at room temperature, rather than in more symmetrical Ge_{2}O_{9} units. At high temperature, the GeO_{5} polyhedra adopt a more trigonal bipyramidal character, and there is an increase in the number of units that can be classified as Ge_{2}O_{9}. This shows that, whilst the high temperature structure retains significant aspects of the low temperature structure, the phase transition leads to increased disorder of the O_{int} oxygens. The less distorted R = Bi material also appears to have a higher proportion of Ge_{2}O_{9}-like groups at low temperature than R = La. This is again correlated to the higher O_{int} disorder caused by a range of local environments.

Previous computational studies have suggested that the most common conduction pathway in La_{10}(GeO_{4})_{6}O_{3} occurs through an interstitialcy mechanism that involves movement of O_{2}− along the c-axis between GeO_{4} units via normal-site O_{2}− and O_{int}. Our experimental local structure analysis results are consistent with this hypothesis and suggest a distribution of sites is present between the GeO_{4} tetrahedra at high temperature. Our static local structure snapshots hence sample the dynamic distribution of atoms that are present in the highly-conducting phases.

In summary, total scattering studies have provided important insight into the local structure rearrangements that occur to accommodate the oxygen interstitial in La_{10}(GeO_{4})_{6}O_{3} and La_{8}Bi_{2}(GeO_{4})_{6}O_{3}, and how these structures re-arrange and become more disordered in the oxygen conducting high temperature phase.

**ASSOCIATED CONTENT**

**Supporting Information.** Supporting information contains: all Rietveld plots discussed in the text; plots of unit cell parameters against temperature for all phases derived from neutron diffraction data; histograms of mode amplitudes and resulting atomic displacements; fits to neutron $F(Q)$ data; histograms of bond lengths and angles at low and high temperature from RMCProfile.
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