Incoherent Bi off-centering in Bi$_2$Ti$_2$O$_6$O’ and Bi$_2$Ru$_2$O$_6$O’: Insulator versus metal

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In the cubic, stoichiometric oxide compounds Bi$_2$Ti$_2$O$_6$O’ (also written Bi$_2$Ti$_2$O$_7$) and Bi$_2$Ru$_2$O$_6$O’ (also written Bi$_2$Ru$_2$O$_7$) Bi$^{3+}$ ions on the pyrochlore A site display a propensity to off-center. Unlike Bi$_2$Ti$_2$O$_6$O’, Bi$_2$Ru$_2$O$_6$O’ is a metal, so it is of interest to ask whether conduction electrons and/or involvement of Bi 6s states at the Fermi energy influence Bi$^{3+}$ displacements. The Bi$^{3+}$ off-centering in Bi$_2$Ti$_2$O$_6$O’ has previously been revealed to be incoherent from detailed by reverse Monte Carlo analysis of total neutron scattering. Similar analysis of Bi$_2$Ru$_2$O$_6$O’ reveals incoherent off-centering as well, but of smaller magnitude and with distinctly different orientational preference. Analysis of the distributions of metal to oxygen distances presented suggests that Bi in both compounds is entirely Bi$^{3+}$. Disorder in Bi$_2$Ti$_2$O$_6$O’ has the effect of stabilizing valence while simultaneously satisfying the steric constraint imposed by the presence of the lone pair of electrons. In Bi$_2$Ru$_2$O$_6$O’, off-centering is not required to satisfy valence, and seems to be driven by the lone pair. Decreased volume of the lone pair may be a result of partial screening by conduction electrons.

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INTRODUCTION

The oxide pyrochlores $A_2B_2O_6O’$, usually abbreviated $A_2B_2O_7$, are well known for their ability to accommodate magnetic cations on interpenetrating sub-lattices of corner-connected $O’/A_2$ tetrahedra and $BO_6$ octahedra. The geometry of the sublattices often result in magnetically frustrated ground states,$^{[1]}$[2] resulting in spin glass, spin ice, or spin liquid phases.$^{[3]}$ Frustration of concerted atomic displacements (dipolar frustration) has also been proposed, when electronic dipoles rather than magnetic spins are placed on the pyrochlore A site.$^{[4]}$[5] with the suggested “charge-ice”$^{[6]}$ displaying the appropriate entropic signatures.$^{[8]}$ Large atomic displacement parameters associated with the A-site cation, seen in Fourier maps of $La_2Zr_2O_7$ and in Bi$_2$M$_2$O$_7$ ($B = Ti, Zn, Nb, Ru, Sn, Hf$),$^{[10]}$[13] contribute to the expanding body of evidence that pyrochlores prefer to accommodate cation off-centering via incoherent disorder rather than in ordered non-cubic ground states.

Among Bi$_2$B$_2$O$_7$ pyrochlores, $B = Ti, (Zn/Nb)$, Sn, and Hf are insulators, while $B = Ru, Rh, Ir$, and Pt are metals.$^{[14]}$ The behavior of Bi$^{3+}$ is suggested to be quite different in insulating and metallic pyrochlores. In insulating Bi$_2$Ti$_2$O$_6$O’ and Bi$_2$Sn$_2$O$_7$ (cubic above 920 K) the Bi is offset by $\sim$0.4 Å from the ideal site. This Bi off-centering is aperiodic, but otherwise analogous to the correlated motion of lone-pair active Bi$^{3+}$ in the ionic conductor Bi$_2$O$_3$.$^{[15]}$ or multiferroic BiFeO$_3$. $^{[16]}$ In metallic pyrochlores, the suggestion is that weaker $A’–O’$ interactions preclude any displacement at all.$^{[17]}$[19] However, Rietveld refinements for compounds where $B = Ru, Rh$, and Ir show that Bi off-centering is still present in experiment.$^{[10]}$[20][22] The short-range correlation of Bi displacements has been probed using reverse Monte Carlo modeling of the diffuse streaks in electron diffraction patterns.$^{[23]}$

In this contribution, we compare structural details in insulating Bi$_2$Ti$_2$O$_6$O’ and metallic Bi$_2$Ru$_2$O$_6$O’ using pair distribution function (PDF) analysis with least-squares and reverse Monte Carlo (RMC) modeling. These techniques reveal the precise structural tendencies of Bi$^{3+}$ off-centering, even in the case of incoherent ice-like disorder.$^{[6]}$ Specific details of bond distances, angles, and real-space shapes can be extracted from the RMC model because it is predicated on fits to the atom-atom distances in the PDF. The work should be placed in the context of ionic off-centering in metallic systems and the screening of ferroelectric dipoles, as first suggested by Anderson and Blount,$^{[23]}$, which finds application in the context of heavily-doped perovskite titanates.$^{[26]}$ We find that the large displacements in Bi$_2$Ti$_2$O$_6$O’ can be reconciled with bond valence analysis, but displacement in Bi$_2$Ru$_2$O$_6$O’ are not driven by valence considerations alone.

To introduce the comparison, Fig.$^{[1]}$ shows that the
scaled heat capacities of Bi$_2$Ti$_2$O$_7$ and Bi$_2$Ru$_2$O$_7$ display pronounced low-temperature humps in plots of $C/T^5$ vs. $T$ that are indicative of local Einstein modes, suggestive of glassy disorder. This large local-mode contribution is largely absent in Y$_2$Ti$_2$O$_7$, which has no lone pair and no experimentally resolvable displacive disorder. Disorder on the O’Bi$_2$ sub-lattice is also seen in the average structure Rietveld refinement of Bragg neutron scattering, masquerading as very large atomic displacement parameters (ADPs) on the Bi sites, displayed as 95% ellipsoids in Fig. 1.

METHODS

Preparation and average structure analysis of Bi$_2$Ti$_2$O$_6$O’ powder used in this study has been reported by Hector and Wiggin. Bi$_2$Ru$_2$O$_6$O’ was prepared as single crystals by Tachibana and finely ground prior to measurement. Time-of-flight (TOF) neutron powder diffraction was collected at the NPDF instrument at Los Alamos National Laboratory at 298 K and 14 K. Rietveld refinement made use of the GSAS code. Extraction of the PDF with PDFGETN used $Q_{\text{max}} = 35$ Å$^{-1}$. Reverse Monte Carlo simulations were run using RMCPROFILE version 6.2. Electronic densities of states (DOS) were calculated by the linear muffin-tin orbital method within the atomic sphere approximation using version 47C of the Stuttgart TB-LMTO-ASA program. Bond valence sums (BVS) were extracted from the RMC supercell as described in previous work on CuMn$_2$O$_4$, using the $R_0$ values of Brese and O’Keeffe.

RESULTS AND DISCUSSION

The total DOS for Bi$_2$Ti$_2$O$_6$O’ and Bi$_2$Ru$_2$O$_6$O’ are shown in Fig. 2(a,b). The features are similar, with metallic Bi$_2$Ru$_2$O$_6$O’ shifted in a nearly rigid-band fashion by approximately 2 eV downward, in agreement with previous work. Partial Bi $s$ and $p$ DOS are shown in Fig. 2(b,c). In both cases, some Bi $s$ states are present at the top of the filled Bi $p$ and $d$ bands. Bi $s$ states are plotted as electron localization function (ELF $\approx 0.65$) isosurfaces at the right of Fig. 2(a,b). With Bi in their ideal 16c positions, the ELFs both show essentially identical circularly averaged lone pairs. Assuming similar lone pair–cation distances, the ELFs imply that both compounds should have the same cation displacement in the real ground state structures.

Time-of-flight neutron diffraction Rietveld refinements at $T = 14$ K and 300 K were performed using the ideal pyrochlore model with Bi on the 16c sites and anisotropic ADPs. Fits at 14 K are shown in Fig. 3. No substantial differences were found from the analysis of Hector and Wiggin or Tachibana et al. including the occupancy: stoichiometric Bi$_2$Ti$_2$O$_6$O’ and a Bi occupancy of 0.97 for Bi$_2$Ru$_2$O$_6$O’. The ADPs from 14 K Rietveld refinement are displayed as 95% ellipsoids in Fig. 1. The
most apparent difference is the larger, disk-shaped ellipsoid representing Bi in Bi$_2$Ti$_2$O$_6$O$'$ and Bi$_2$Ru$_2$O$_6$O$'$.

The Bi clouds are viewed normal to the $O'$–Bi–$O'$ bond. The large anisotropic ADPs of Bi envelop this ring. A split Bi position can give a better fit to the diffraction data. The previous study found that there is a slight tendency for Bi to prefer the 96$h$ positions. This represents a six-fold splitting of the Bi into sites that are displaced $\sim 0.4$ Å from the ideal site, and pointing between nearby O ions on 48$f$ sites. Bi ADPs in Bi$_2$Ru$_2$O$_6$O$'$ also suggest displacive disorder. They too are anisotropic and appear as slightly flattened ellipses in Fig. 4.

The most straightforward way to compare the Rietveld-refined unit cell with the local structure is via least-squares PDF refinements, shown in Fig. 4. Two issues should be considered. First, the fit for Bi$_2$Ti$_2$O$_6$O$'$ is significantly worse overall than Bi$_2$Ru$_2$O$_6$O$'$. This implies that the local structure of Bi$_2$Ti$_2$O$_6$O$'$ is more poorly described by the $F\bar{4}m$ unit cell. Second, the fit for Bi$_2$Ti$_2$O$_6$O$'$ is poorest at low $r$, which contains details of near-neighbor atomic distances (of particular importance are Bi–O and Bi–$O'$), and is still unsatisfactory at higher $r$ even though a larger number of pairs are being included. The fit for Bi$_2$Ru$_2$O$_6$O$'$ is equally decent at all $r$ values up to 20 Å.

These PDF fits do not give the positions of atoms in either compound, but they quickly reveal valuable information about the presence of local atomic displacements (more apparent in Bi$_2$Ti$_2$O$_6$O$'$ than Bi$_2$Ru$_2$O$_6$O$'$) and the correlations between them (still unable to be averaged for $r < 20$ Å). Extracting structural tendencies of geometrically frustrated compounds via least-squares refinement is inherently difficult because there is no straightforward way to model the large, complex collection of discrete displacements needed to reproduce the disorder. Least-squares is not a suitable algorithm for determining so many free Bi positions, especially when their interactions may be correlated. Instead, we remove symmetry constraints and use RMC to investigate how Bi are distributed within a large supercell.

Simulations were carried out using the RMC method to investigate the precise positions of Bi. Simultaneous fits to the PDF and Bragg profile for Bi$_2$Ru$_2$O$_6$O$'$ are shown in Fig. 5. Unit-cell based modeling (least-squares refinements, including Rietveld) usually fails to model incoherent static displacements. In contrast, each RMC supercell contains thousands of ions of each type. Folding the RMC supercell into a single unit cell produces “point clouds” of ions at each crystallographic site. These clouds display the propensity of ions to displace from their ideal positions. The mean squared displacement of points are in quantitative agreement with the average ADPs obtained from Rietveld refinement. Mapping these points as two-dimensional histograms (Fig. 6) shows the tendency of Bi nuclei to offset in Bi$_2$Ti$_2$O$_6$O$'$ and Bi$_2$Ru$_2$O$_6$O$'$. The Bi clouds are viewed normal to

FIG. 3. (Color online) Time-of-flight neutron diffraction Rietveld refinement of Bi$_2$Ti$_2$O$_6$O$'$ (top) and Bi$_2$Ru$_2$O$_6$O$'$ (bottom) at 14 K using the ideal pyrochlore structure with anisotropic thermal parameters. The fit to Bi$_2$Ti$_2$O$_6$O$'$ is visibly worse due to large amounts of diffuse shoulder intensity. This diffuse scattering is a result of large local Bi and $O'$ displacements.

FIG. 4. (Color online) Least-squares PDF fits (using the unit cell from Rietveld refinement) do not reproduce the low-$r$ structure of Bi$_2$Ti$_2$O$_6$O$'$ due to the inability of a unit-cell based description to accommodate incoherent static displacements. The fit to Bi$_2$Ru$_2$O$_6$O$'$ is significantly better because the static displacements are smaller.
the O′–Bi–O′ bond (top) and perpendicular (bottom) for two temperatures.

The Bi ring in Bi$_2$Ti$_2$O$_6$O′ is evident from Fig. 6 and has a diameter of ~0.8 Å. At 300 K, the ring is more diffuse. We attribute this to thermal broadening. Interestingly, the ring is not a perfect circle. It has a sixfold symmetry corresponding to the preference for Bi to occupy the 96h positions (corners of the hexagon), which point between the six neighboring 48f O ions in the TiO$_6$ network. [6]

The Bi distribution in Bi$_2$Ru$_2$O$_6$O′ is distinctly different, but static displacement is still present. The displacements are densely clustered close to the ideal position and there is no hollow center as in Bi$_2$Ti$_2$O$_6$O′. However, the perpendicular view reveals that the Bi distribution is still disk-shaped. Most surprising is the symmetry of the disk. It also has a hexagonal shape but the hexagon is rotated 30° with respect to what is seen in Bi$_2$Ti$_2$O$_6$O′, with flat edges on the left and right, and corners on the top and bottom. This implies that Bi is displacing toward the nearby 48f O onto 96g positions. The Bi offset roughly agrees with the value of 0.16 Å found in the split-site model of Avdeev. [10]

Quantitative RMC Bi nuclear density as a function of the angle θ around a ring normal to the O′–Bi–O′ bonds is shown in Fig. 6b,c. Both compounds show sixfold modulation fit by a cosine curve with a period of 60°, but their oscillations are offset by 30°.

Bond valence sums are calculated for each individual cation in the supercell and plotted as histograms in Fig. 7 for (a) Bi$_2$Ti$_2$O$_6$O′ and (b) Bi$_2$Ru$_2$O$_6$O′ at $T = 14$ and 300 K. In all cases, BVS distributions are centered on the expected valence: Bi$^{5+}$, Ti$^{4+}$, Ru$^{4+}$, and O$^{2−}$. A slight sharpening is seen for the low-temperature measurement. These distributions reveal that the RMC simulations contain chemically reasonable bond lengths despite the absence of such distance constraints in the simulations. They also reveal that there is no tendency for Bi$^{5+}$ in Bi$_2$Ru$_2$O$_6$O′, supporting the conclusion from LMTO calculations that Bi 5s states are localized far below the Fermi energy.

The calculated Bi BVS versus displacement in Fig. 7c demonstrates why displacements are more pronounced in Bi$_2$Ti$_2$O$_6$O′. In the average structures, Bi$_2$Ti$_2$O$_6$O′ and Bi$_2$Ru$_2$O$_6$O′ respectively obtain only 1.31+ and 1.38+ per Bi from bonds to O′. The majority of the valence is obtained from 48f O and increases with Bi displacement, represented by the upward curve. Bi in both compounds gain about the same valence from 48f O but a large displacement is required to reach the retracted Ti$_2$O$_6$ sublattice. The result is that each Bi in Bi$_2$Ti$_2$O$_6$O′ gains an uneven amount of charge from the six 48f O, locking in dipoles. This explains why the Bi displacements appear to be static in variable temperature measurements. [6]

The rigidity of the BiO$_6$ sublattice is confirmed by small ADPs on 48f O in both compounds, even in the presence...
of nearby Bi offcentering. In Bi$_2$Ru$_2$O$_6$O’, the Ru$_2$O$_6$ network pushes 48f O closer to Bi so that valence is satisfied.

We have considered whether covalency could lead to difficulties in using BVS to judge valence in Bi$_2$Ru$_2$O$_6$O’: should more covalent bonding (shorter M–O bonds) lead to Bi and Ru requiring more than the formal 3+ and 4+ to be satisfied? This seems unlikely, not only because Rietveld refinement and RMC find the desired states centered near the nominal values. The average structure of semiconducting BiCaRu$_2$O$_7$ [34] displays much higher BVS sums (3.25+ for Bi, 4.20+ for Ru) than Bi$_2$Ru$_2$O$_6$O’, but large anisotropic ADPs on the A site portend static disorder nonetheless.

In Bi$_2$Ti$_2$O$_6$O’, off-centering helps satisfy Bi valence and the lone pair can be accommodated in the opposite direction. In Bi$_2$Ru$_2$O$_6$O’, no off-centering is necessary from valence considerations, so static disorder may be driven by lone-pair activity. Metallic screening in Bi$_2$Ru$_2$O$_6$O’ is expected to decrease repulsions of the lone pair from nearby O, [21] allowing Bi to stay closer to the ideal position than the traditional cation–lone pair distance would dictate. This is supported by the idea that lone pairs often exhibit decreased volumes. [35]

**CONCLUSIONS**

In conclusion, reverse Monte Carlo structural analysis using total neutron scattering provides a detailed view of the incoherent static displacements in Bi$_2$Ti$_2$O$_6$O’ and Bi$_2$Ru$_2$O$_6$O’. Real-space maps of static displacements reveal the distinct magnitudes and directions of Bi off-centering in Bi$_2$Ti$_2$O$_6$O’ and Bi$_2$Ru$_2$O$_6$O’. While static displacements in the insulator Bi$_2$Ti$_2$O$_6$O’ can be understood on the basis of valence satisfaction alone, the cause for displacements in metallic Bi$_2$Ru$_2$O$_6$O’ is not captured by first-principles calculations on the ideal compound or by the bond valence sum. An incoherent lone-pair driven distortion is present but is partially screened by the conduction electrons.

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