are perforce associated with non-cubic symmetries.[12] Diffuse intensity in electron diffraction patterns of related compounds including $Bi_2Ru_2O_7$, Bi_2InNbO_7, and Bi_2ScNbO_7 may indicate short-range correlations in the Bi displacements.[13–15] If Bi displacements cooperatively order with each other, they must do so only over short ranges. Crystallographic analysis based on Bragg scattering leaves a void in the ability to probe such short-range order, as analyses are predicated on the existence of long-range order. Consequently, studies of displacive disorder on the A site *via* Rietveld refinement or Fourier maps can produce a model of the *average* electron or nuclear distributions, but each A site has an identical cloud of intensity.[16]

We investigate models where the correlated motion of atoms on the A sites reproduces the atomistic, pairwise distances between individual atoms. This description is provided by an appropriate Fourier transform of the total scattering function $S(Q)$ to provide a normalized pair distribution function (PDF).[17,18] In this study, the PDF and the Bragg profile are used as experimental constraints in a large-box (11,000 atom) model of $Bi_2Ti_2O_6O'$ to obtain, using reverse Monte-Carlo (RMC) analysis, a consistent picture of the the coordination tendencies of all atoms. Many of these models are combined and used as a set of atomic positions for further analysis. RMC compares the experimental and computed (based on atom positions in the simulation box) $D(r)$ and $S(Q)$ while randomly relaxing atomic positions. The method is similar to Metropolis Monte Carlo, except that the fit to data χ^2, instead of a potential energy function, is minimized.[19–21]

There are many approaches to describing the behavior and correlations of atomic positions as obtained from large-box models of structure. Some examples include the use of quadrupolar moments of octahedra to describe $LaMnO_3$,[22] of contour plots of bond angles in cristobalite,[23] and the use of bond valence analysis to obtain valence states from a statistical analysis of metal-oxygen positions.[24,25] Here we analyze the local geometry using simple metrics, then present the continuous symmetry measures (CSM)[26–28] of polyhedra from RMC simulations. The CSM model provides a quantitative measure of a polyhedron's distortion, in the form of a "distance" from ideality. A key advantage of CSM is its ability to compare shapes in different compounds.[28] The CSM has been used to correlate deviations from ideal tetrahedra in silicates as a function of applied pressure,[29] and to analyze second-order Jahn-Teller systems across a variety of crystal structures.[30] In these cases, the CSM was considered for the average crystallographic stucture, *e.g.* one where polyhedra possess a single CSM value. Here, we extend CSM to large-box modeling by calculating it for every $O'Bi_4$ tetrahedron in the RMC supercell, obtaining distributions, rather than single values.

The key finding to emerge from this study is that displacements from ideal atomic positions in $Bi_2Ti_2O_6O'$ and in particular, the nature of the $O'Bi_4$ tetrahedra indicate a tendency for Bi to lie in a disordered ring around the ideal position, with some preference for near-neighbor Bi-Bi ordering. This reaffirms the case that, even when probed microscopically, $Bi_2Ti_2O_6O'$ is ice-like in its disorder. We emphasize that in drawing the analogy with ice, we do not suggest the existence of ice-rules of the Bernal-Fowler[31] type in these systems.

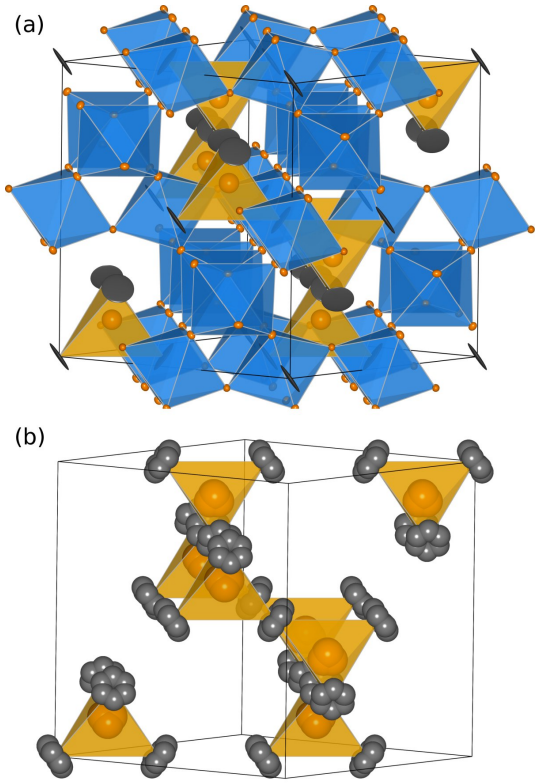

FIG. 1: (Color online) The $Bi_2Ti_2O_6O'$ crystal structure is shown in (a), with 50% thermal ellipsoids representing the atomic displacement parameters from Rietveld refinement at 14 K. The two sublattices are corner-sharing TiO_6 octahedra (blue) and corner-sharing $O'Bi_4$ tetrahedra (orange). Bi and O' are on ideal positions. Bi cations (black) appear as discs due to their displacement normal to the O'–Bi–O' bond. This disorder can be modeled using six-fold-split Bi and four-fold-split O' as shown in (b) (only the $O'Bi_4$ is sublattice shown).

II. METHODS

Synthesis and a detailed average structural analysis of the sample used in this study (including verification of purity) has been reported by Hector and Wiggin.[9] Briefly, a basic solution of titanium metal with hydrogen peroxide and ammonia was added to an acidic solution of bismuth nitrate pentahydrate and nitric acid. The resulting precipitate was filtered, washed with a dilute ammonia solution, dried at 50°C, and calcined in air for 16 h at 470°C. Time-of-flight (TOF) neutron powder diffraction on samples held in vanadium cans was collected at the NPDF instrument at Los Alamos National Laboratory at 298 K