An Exhaustive Symmetry Approach to Structure Determination: Phase Transitions in Bi$_2$Sn$_2$O$_7$

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Supporting Information

ABSTRACT: The exploitable properties of many materials are intimately linked to symmetry-lowering structural phase transitions. We present an automated and exhaustive symmetry-mode method for systematically exploring and solving such structures which will be widely applicable to a range of functional materials. We exemplify the method with an investigation of the Bi$_2$Sn$_2$O$_7$ pyrochlore, which has been shown to undergo transitions from a parent $\gamma$ cubic phase to $\alpha$ and $\beta$ structures on cooling. The results include the first reliable structural model for $\beta$-Bi$_2$Sn$_2$O$_7$ (orthorhombic $Aba2$, $a = 7.571833(8)$, $b = 21.41262(2)$, and $c = 15.132459(14)$ Å) and a much simpler description of $\alpha$-Bi$_2$Sn$_2$O$_7$ (monoclinic $Cc$, $a = 13.15493(6)$, $b = 7.54118(4)$, and $c = 15.07672(7)$ Å, $\alpha = 125.0120(3)$°) than has been presented previously. We use the symmetry-mode basis to describe the phase transition in terms of coupled rotations of the BiO$^-$ anti-cristobalite framework, which allow Bi atoms to adopt low-symmetry coordination environments favored by lone-pair cations.

INTRODUCTION

Many functional materials have exploitable properties that are intimately associated with symmetry-lowering phase transitions induced as a function of an external variable such as temperature, pressure, or chemical composition. Typical examples include materials showing one of the ferroic orders (ferroelectric, ferromagnetic, and ferroelastic), second harmonic generation (SHG) switches, positive-to-negative thermal expansion changes, and structurally induced insulator to metal/superconductor transitions. Such transitions can lead to complex superstructures which can be difficult to determine using conventional characterization approaches, particularly when only polycrystalline samples are available. Here we describe an exhaustive approach using symmetry-adapted distortion modes (which we refer to as “symmetry modes”) and automatically generated group-subgroup trees which we believe will be widely applicable to such problems. We demonstrate the approach on pyrochlore-type Bi$_2$Sn$_2$O$_7$, the structural chemistry of which has been the subject of considerable debate. Our approach allows us to systematically determine and describe what we believe are definitive structural models for the $\alpha$, $\beta$, and $\gamma$-phases, and resolve their conflicting descriptions in the literature.

Pyrochlore structures have been widely studied due to the range of important properties they exhibit, including ferroelectricity, dielectric properties, superconductivity, oxide-ion conductivity, colossal magnetoresistance (CMR), CO sensing, metal-semiconductor transitions, spin-ice magnetic frustration, radio-isotope isolation, and photocatalysis. Materials with the ideal pyrochlore structure crystallize in space group $Fd\bar{3}m$ and have general formula A$_2$B$_2$O$_6$O$^-$ (Figure 1). With origin choice 2, A cations (generally 2+ or 3+) occupy 16$c$ positions, B cations (generally 4+ or 5+) occupy 16$d$ positions, O anions occupy 48$f$ sites, and O$^-$ anions occupy 8$a$ sites. There is a single freely refineable atomic coordinate: the $x$ coordinate of O. It is often helpful to think of the pyrochlore structure as interpenetrating A$_2$O$^-$ and B$_2$O$_6$ frameworks. The A$_2$O$^-$ framework contains corner-sharing A$_2$O$_3$ tetrahedra with the anti-cristobalite arrangement, and the B$_2$O$_6$ framework contains corner-sharing BO$_{12}$ octahedra. The interpenetration of the two frameworks leads to A cations having a distorted hexagonal bipyramidal coordination environment: AO$_6$O$^-$/2, typically with six longer equatorial bonds arranged in a puckered hexagon and shorter axial bonds.

There has been significant interest in pyrochlores with Bi(III) on the A site, where the stereochemically active Bi lone pair leads to it moving away from its high-symmetry coordination environment. In Bi$_2$Ti$_3$O$_7$, first synthesized and characterized by Radosavljevic et al., Rietveld refinement suggests Bi displacement to 96$h$ sites (toward a hexagon edge) rather than to 96$g$ sites (directly toward an oxygen or hexagon corner). Subsequent Pair Distribution Function (PDF) studies also concluded that Bi positions are preferentially displaced to 96$h$, with short-range correlations of BiO tetrahedral displacements. The frustration of long-range coherent off-center displacements of Bi was discussed by Seshadri as being responsible for preventing a paraelectric-ferroelectric phase transition.

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transition. The term “charge ice” has been coined in analogy to the “spin ice” properties of materials such as Dy2Ti2O7 and Ho2Ti2O7. Other examples include the electrocatalyst B14Ru2O4, where simulation of diffuse scattering in electron-diffraction data points to distortions of Bi positions in a disc similar to that observed for B14Ti2O4. Wang et al. have discussed the influence of B-site covalency on Bi distortions in pyrochlore bismuth zinc niobates and suggested that more-ionic B sites (e.g., Sn, Ti) are more likely to distort from cubic symmetry. Local bonding requirements, distortions, and cation order are also known to be important in controlling dielectric properties of materials such as B14(Zn1/3Nb2/3)2O7.

Bi2Sn2O7 has shown potential for technological applications in catalytic oxidation of isobutene, methane coupling, and selective carbon monoxide sensing. It was first reported by Roth in 1956 as having a diffraction pattern similar to that of cubic pyrochlores but with additional peaks pointing to a distorted structure. The first report of polymorphism in Bi2Sn2O7 was given by Shannon and co-workers. They described three pyrochlore-related forms: a high-temperature (>900 K) γ-phase, an intermediate-temperature (390–900 K) β-phase, and a low-temperature α-phase, all with pyrochlore-related structures. The transition from γ to β was reported as second order, and both the α- and β-phases were SHG active. The high-temperature γ-form is relatively uncontroversial. Its average structure is that of a cubic pyrochlore with a=10.73 Å, though with local distortions due to Bi(III) ions moving off the ideal pyrochlore site.

The intermediate β-Bi2Sn2O7 was reported as being face-centered-cubic with a=21.4 Å (2a_abc), and room-temperature α-Bi2Sn2O7 as body-centered tetragonal with a=b=15.14 Å and c=21.4 Å (√2a_abc √2a_abc 2a_abc). Despite attempts by several groups, no reliable structures for α- or β-Bi2Sn2O7 were reported until Evans et al. performed an exhaustive study of the 21 different structures possible for α-Bi2Sn2O7 based on three assumptions that α, β, and γ follow group-subgroup relationships; that β has a yet-unknown and apparently cubic structure with a cell edge of 2a_abc; and that α and β are SHG active. They concluded that, under these assumptions, the distortion data of α-Bi2Sn2O7 could only be accurately described using a monoclinic P21 structure with 176 crystallographically unique atoms. For clarity we refer to this model as α-Bi2Sn2O7 throughout this paper. New experimental studies on β-Bi2Sn2O7 by us and others have revealed additional weak reflections and peak splittings inconsistent with a face-centered cubic cell, indicating lower symmetry. Salamat et al. proposed a β-Bi2Sn2O7 model in space group P31, with cell parameters of a=7.35 (a_abc/√2) and c=37.01 Å (2√3a_abc) which was metrically cubic and has a cell volume of 1.5 × V_{cub}. However, this model does not fit high-resolution powder diffraction data from the β-phase and shows no obvious symmetry relationship to the α or γ forms, suggesting that it needs revisiting.

The new experimental observations on β-Bi2Sn2O7 clearly invalidate some of the assumptions used to determine the α-Bi2Sn2O7 model of α-Bi2Sn2O7. This, and insight from the symmetry-mode analysis discussed below, has prompted us to also revisit the structural chemistry of both α- and β-Bi2Sn2O7. To allow a systematic exploration of all the possible structures for the α- and β-phases, we report an automated exhaustive approach for producing candidate models, generating their symmetry-mode parameterizations, and performing combined symmetry-mode refinements against X-ray and neutron diffraction data sets. This approach allows us to identify a simpler structural description for α-Bi2Sn2O7, and a new structural model for β-Bi2Sn2O7. We describe the important local structural distortions in each phase and the structural relationships between them.

The method we report allows a systematic and exhaustive search of the structural landscape accessible following a symmetry-changing phase transition. We therefore believe that the approach is broadly applicable and will be of significant importance in the study of a wide range of functional materials.

### EXPERIMENTAL SECTION

Bi2Sn2O7 was prepared from stoichiometric quantities of Bi2O3 (1.214 g, 2.61 mmol) and SnO2 (0.786 g, 5.22 mmol) which were intimately ground in a mortar and pestle and fired at 1373 K for 16 h. Powder diffraction indicated formation of a single-phase product. The sample was reheated to 1223 K immediately prior to synchrotron and neutron powder diffraction experiments. Synchrotron X-ray data were collected at the Diamond 111 beamline on a sample loaded in a 0.3 mm capillary from 2° to 140° for 2 h at 293 K and 4 h at 470 K using a wavelength of 0.8264 Å and high-resolution multi-analyzer crystal (MAC) detectors. Rapid data collections were performed from 250 to 470 K using a data collection time of 2 min per scan. Neutron diffraction data were collected on the high-resolution powder diffractometer HRPD at ISIS over a time-of-flight range of 30–130 ms at 298 and 473 K with total data collection times of 8 h (250 μAh).

To undertake the structural work reported in this paper, a new feature was added to the ISODISTORT software package which outputs an exhaustive listing of the intermediate structures that fall...
between a parent structure and a distorted child structure, i.e., the structures whose symmetry groups are intermediate to the parent and child symmetry groups. Multiple domains of a given subgroup are treated as duplicates, so that only one domain of each subgroup is listed in the tree. In addition to a variety of useful descriptive information (e.g., space group, sublattice basis and origin, cell parameters, symmetry index, etc.), ISODISTORT automatically generates a symmetry-mode parameterization of each structure from information (e.g., space group, sublattice basis and origin, cell parameters) listed in the tree. In addition to a variety of useful descriptive information, X-ray and neutron data were simultaneously fitted to \( d_{\text{min}} = 0.7 \, \text{Å} \). Instrumental contributions to peak shapes and the X-ray wavelength were determined from LaB6 and Si/CeO2 standards for synchrotron and neutron data, respectively. Absorption corrections were refined using room-temperature data. For the \( \beta \)-phase we refined a total of 64 mode amplitudes, 3 cell parameters, and 4 isotropic temperature factors (equating Bi-, Sn-, O-, and O′-derived sites of the parent) for the 24 symmetry-independent atoms, though one \( \Gamma^\prime \) mode was set at zero to fix the origin. An additional 50 parameters were used to describe background, peak shape and other experimental effects. For the \( \alpha \)-phase, 66 mode amplitudes (22 unique atoms) were refined, two of which fixed the origin. The \( \alpha \)-phase peaks are significantly broader than those of the \( \beta \)-phase and also show a slight hkl-dependent width and asymmetry (see Figure 6 and SI Figure S2). We therefore introduced a Stephens-type strain broadening for final refinements giving \( R_{wp} \approx 5.6 \% \). Strain broadening is unsurprising given the significant cell-metric change (\( \Delta d/d \approx 1 \times 10^{-5} \)) which occurs at the first-order \( \beta \)-to \( \alpha \)-phase transition at 390 K. An excellent fit reproducing the observed asymmetry can also be achieved using a multi-phase model where the cell parameters and phase fractions of a set of structurally identical phases are parameterized to describe the strain broadening. Only six parameters are required in this approach, and a lower \( R_{wp} \) is obtained than with the Stephens approach (4.9%) (SI Figure S2). Both models result in essentially identical refined-mode amplitudes. Effective polyhedral tilt angles in each final structure were determined using GASP.51,52

## RESULTS AND DISCUSSION

### Variable-Temperature Diffraction Data and the \( \alpha_{\text{BCS}} \)

#### Bi2Sn2O7 Model.

High-resolution synchrotron X-ray and neutron (\( \Delta d/d \approx 10^{-4} \, \text{Å} \)) powder diffraction data were collected up to 473 K on Bi2Sn2O7. Despite being derived from...
medium resolution powder data ($\Delta d/d \approx 10^{-2}$ Å), the published $Pc$ $\alpha_{dil}$-$Bi$_2$Sn$_2$O$_7$ structure gave an essentially flawless fit to room-temperature high-resolution data without refining any structural parameters. Refinement of the model against variable-temperature diffraction data gave clear evidence for the first-order phase transition to $\beta$-$Bi$_2$Sn$_2$O$_7$ at 390 K (Figure 2). The monoclinic cell angle freely refined to 89.995(1)° (i.e., 90° to the true precision of the experiment) for the $\beta$-phase. From neutron data the $\beta$ cell appears metrically cubic, but the higher resolution X-ray data reveal small peak splittings, suggesting lower metric symmetry (Figure 2b). The idea that the $\alpha$-phase structure descends in symmetry from a face-centered-cubic $\beta$-phase structure was a key literature-based assumption in the 2003 derivation of the $\alpha_{dil}$ model of $\alpha$-$Bi$_2$Sn$_2$O$_7$, which is therefore incorrect.

In addition, our $\beta$-phase diffraction data show weak superstructure reflections at the X point in reciprocal space, which are not present in the $\alpha$ data. It is interesting that these superlattice reflections can be adequately fitted when the $\alpha_{dil}$-$Bi$_2$Sn$_2$O$_7$ model is refined against the $\sim$473 K $\beta$-phase data, but have zero calculated and observed intensity when it is refined against $\alpha$-phase data at room temperature (Figure S3). These observations suggest that a simpler model may be possible for $\alpha$-$Bi$_2$Sn$_2$O$_7$, and that the $\alpha_{dil}$ model may actually be a common isotropy subgroup of both the correct $\alpha$- and $\beta$-phase structures.

Lattices of the $\beta$- and $\alpha$-$Bi$_2$Sn$_2$O$_7$ Superstructures. Experimentally, we observe that all the clearly separable superlattice peaks in the powder diffraction data of either the $\alpha$- or $\beta$-phases are associated with the $L$ or $X$ points in reciprocal space (see Figure S3). Assuming that we have not missed any points, we can superpose the most general $L$- and $X$-point order-parameter directions to obtain a $P1$ symmetry superstructure with cell parameters of $a \approx b \approx c \approx 15.14$ Å, $\alpha \approx \beta \approx \gamma \approx 90^\circ$, and $V \approx 4V_{sub}$. The superstructure must have sufficient degrees of freedom to capture any structural features of either the $\alpha$- or $\beta$-phases. For this work, we further opted to double the cell volume according to $a = b = 15.14$ Å, $c = 21.48$ Å, $\alpha \approx \beta \approx \gamma \approx 90^\circ$, and $V \approx 4V_{sub}$ in order to keep the larger $\alpha_{dil}$-$Bi$_2$Sn$_2$O$_7$ model within the scope of our analysis. The primary hypothesis in our present exploration of possible superstructures for $\alpha$- and $\beta$-$Bi$_2$Sn$_2$O$_7$ is that their isotropy subgroups must be supergroups of this “base” structure and subgroups of the “parent” $\gamma$-phase structure. The collection of all such candidates comprise a “tree” of intermediate subgroups.

A newly released subgroup tree feature in ISODISTORT was used to generate an exhaustive list of distinct intermediate subgroups that are both subgroups of the parent $\gamma$-phase symmetry and supergroups of the base $P1$ subgroup. A total of 547 distinct candidate subgroups are predicted, each with a corresponding refinable structural model. Of these, two are incapable of supporting atomic displacements beyond those of

Figure 3. Lattice—sublattice relationships among the 14 lattice subgroups extracted from the tree of 547 intermediate subgroups. For each entry, the first line shows the subgroup candidate number and the cell volume (relative to that of the primitive parent cell, $V_p = 224$ Å$^3$); the second line indicates the active k-vectors; the third line shows the unit cell parameters ($a/\alpha_{dil}$, $b/\alpha_{dil}$, $c/\alpha_{dil}$, $\alpha$, $\beta$, $\gamma$), with edge lengths presented relative to the cubic parent ($a_{dil} = 10.72$ Å) and angles in degrees. A given lattice is linked to each of its minimal superlattices and maximal sublattices with a solid line. Active k-vectors are numbered corresponding to their positions in Table 1. For example, the set of active k-vectors of lattice subgroup #184 includes the only arm of the star of GM, the second and third of four arms of the star of $L$, and the third of three arms of the star of $X$. At minimum, the set of active k-vectors of a given lattice must contain all of the active k-vectors of each of its maximal superlattices, though it will generally contain other k-vectors too. The lattice subgroups found for $\alpha$- and $\beta$-$Bi$_2$Sn$_2$O$_7$ are shown in red and blue boxes, respectively.
For each type of reciprocal-space \( k \)-vector from this list. Lattice subgroups above the red and blue lines have suitable candidate models. We refer to this set of 14 parent lattices as the correct lattice subgroups for \( \alpha \)- and \( \beta \)-phase, each of the lattice subgroups in the 547-member tree are associated with exactly one of these 14 lattice subgroups. Because a lattice subgroup combines all of the structural information of all of the candidate models associated with it, a model based on the lattice subgroup will fit the observed diffraction data at least as well as any of the associated candidate models.

The correct lattice subgroups for \( \alpha \)- and \( \beta \)-Bi\(_2\)Sn\(_2\)O\(_7\) were identified by testing all 14 of them against diffraction data from both phases using the RLM Rietveld approach described in the Experimental Section. \( R_{wp} \) values for each of these joint neutron/X-ray fits are included in Table 1, which is ordered according to how well candidates fit the \( \beta \)-phase data. Table 1 also lists the active \( k \)-vectors for each subgroup. For \( \beta \)-Bi\(_2\)Sn\(_2\)O\(_7\), we see a clear break in \( R_{wp} \) from \( >19\% \) to \( \leq 4.7\% \), for lattice subgroups that possess \( L \)-point modes, and a second smaller but significant break from \( \sim 4.7\% \) to \( \leq 4.3\% \) when \( X \)-point modes become available (the first 5 rows of Table 1, above the blue line). We see that lattice subgroup #184 provides an excellent fit to the data, which has a relatively low parameter count (264), and excludes contributions from reciprocal-space points for which we see no evidence of superlattice reflections (i.e., \( \Delta, \Sigma, W \)). It is the clear choice for the primitive lattice of the \( \beta \)-phase. Because the candidate models associated with a given lattice subgroup appear continguously in ISODISTORT’s subgroup-tree listing (SI Table S1), we can now isolate the \( \beta \)-phase subgroup to lie somewhere on or between candidates #145 and #184 in our tree.

For the \( \alpha \)-phase, each of the lattice subgroups in the first six rows of Table 1 (above the red line) give an excellent fit to the diffraction data, demonstrating that only \( L \)-point modes contribute to the structure, consistent with visual inspections of the clearly separable superlattice reflections. Following the same arguments used for \( \beta \), we see that lattice subgroup #93 is the clearly separable superlattice reflections. Following the same arguments used for \( \beta \), we see that lattice subgroup #93 is the clear choice for the \( \alpha \)-phase. The other lattices that lie above the red line in Table 1 are sublattices of #93; we judge that their fits are slightly better only because of their greater parameter counts (see below). The correct \( \alpha \)-phase subgroup must then lie on or between candidates #72 and #93 in our tree. We note that the \( \beta \)-phase lattice (184) is a maximal sublattice of the primitive \( \alpha \)-phase lattice (93), and has double the primitive cell volume.

**Exhaustive Subgroup Search.** For the \( \beta \) - and \( \alpha \)-phases, identification of the lattice subgroup restricts the number of candidate models that need to be tested to 40 and 22 respectively. However, in this section we choose to test all 547 candidate models. We do this for three reasons: completeness in this proof-of-concept study; because for this example, it is not much more computationally demanding than testing just the \( \alpha \)-phase data respectively. In this proof-of-concept study; because for this example, it is not much more computationally demanding than testing just the \( \alpha \)-phase data respectively. In this proof-of-concept study; because for this example, it is not much more computationally demanding than testing just the \( \alpha \)-phase data respectively. In this proof-of-concept study; because for this example, it is not much more computationally demanding than testing just the \( \alpha \)-phase data respectively. In this proof-of-concept study; because for this example, it is not much more computationally demanding than testing just the \( \alpha \)-phase data respectively.
Figure 4. Final $R_{wp}$ values from refinements of the 547 candidate models for $\beta$-Bi$_2$Sn$_2$O$_7$ against ~737 K X-ray and neutron diffraction data. Individual panels show (a) all $R_{wp}$ values as a function of child candidate number in the tree, (b) $R_{wp}$ as a function of the number of refined parameters for the 80 lowest-$R_{wp}$ candidates, (c) $R_{wp}$ values for all candidates in ranked order, and (d) the 80 lowest-$R_{wp}$ candidates in ranked order. “Best” candidates lie toward the bottom left-hand corner of panel b. Candidate #152 (our best β-structure model) is marked with a red circle, and candidate #88 (our best α-structure model) is marked with a blue square.

Figure 5. Final $R_{wp}$ values from refinements of the 547 candidate models for α-Bi$_2$Sn$_2$O$_7$ against ~293 K X-ray and neutron diffraction data. Individual panels are α-phase equivalents to those in Figure 4. Candidate #152 (our best β-structure model) is marked with a red circle, and candidate #88 (our best α-structure model) is marked with a blue square.

Similar conclusions can be drawn from the equivalent plots for the α-phase shown in Figure 5. In Figure 5a,c, we see that candidate models fall into two broad categories with $R_{wp}$ ≤ 25% and $R_{wp}$ ≥ 37%. This break is associated with a single essential $\Gamma_1^\alpha$ mode. Focusing on the best candidates (Figure 5d), the drop in $R_{wp}$ value at the 16th-ranked candidate (blue square) is associated with the switching on of an essential $\Gamma_2^\alpha$ mode, at which point all active modes are included. Lower-$R_{wp}$ candidates have additional $\Delta_\gamma$, $\Sigma_\gamma$, $X_\gamma$, and W-point modes, which are not needed to adequately fit the data. The plot of $R_{wp}$ against the number of structural parameters (Figure 5b) therefore shows that #88 ($C_\gamma$, $R_{wp}$ = 7.94%, 16th in rank, 72 parameters, marked with a blue square) is the standout candidate; its monoclinic cell parameters are $a = 13.15$, $b = 7.54$, $c = 13.14$, $\beta = 110^\circ$ ($\sqrt{3}/2 a_{\text{cel}}$, $a_{\text{cel}}/\sqrt{2}$, $\sqrt{3}/2 a_{\text{cel}}$) and it gives an excellent fit to the data. The second-best candidate is one of #173 and #174 (see Table S2), which both have P$\gamma$ symmetry on the same lattice and approximately twice the number of refineable parameters as #88. A Hamilton test again confirms #88 as the best model for the α-phase, and examination of the Rietveld profiles shows that all the extra reflections predicted by larger-cell low-$R_{wp}$ models have zero observed intensity.

Structural Discussion. Our exhaustive subgroup search suggests relatively simple models for both β- and α-Bi$_2$Sn$_2$O$_7$. Full Rietveld refinements for each give excellent fits to the experimental data (Figure 6). Refinement details, important bond distances, and bond valence sums are included in Tables 2 and 3.

For the β-phase we highlight the small splitting of the (4 8 0) and (0 8 8) reflections at $d$ ≈ 1.55 Å, characteristic of the small deviation from a metrically cubic cell ($\Delta d/d < 5 \times 10^{-4}$ inset to Figure 6a). This splitting is a good differentiator among the various intermediate lattices in the tree. We also see excellent agreement with weak peaks at the X-point (Figure S3), which are visible in the diffraction pattern of β- but not α-Bi$_2$Sn$_2$O$_7$.

We can gain insight into the important structural distortions of the β- and α-phases from the refined symmetry-mode amplitudes. Direct comparison of the two structures is complicated by the absence of a group—subgroup relationship between them. It is, however, possible to compare them by
transforming each to their highest common subgroup, candidate #174 (see SI for details). #174 (space group $Pc$) is a subgroup of index 2 for both models; it has the same lattice as $\beta$, and the same point group as $\alpha$. Figure 7 compares non-zero-mode amplitudes in this common subgroup. Note that some modes get split in two in the subgroup, e.g., the $L_2^1(a,0,0,0)$ mode of $\beta$ (#152) splits into the separate $a$ and $b$ branches of $L_2^1(a,b,0,0)$ in #174 with $b = -a$.

The 534-parameter $\alpha$-old-Bi$_2$Sn$_2$O$_7$ model (candidate #537, lattice subgroup #547) also proves to be a common subgroup of the new $\alpha$ (#88) and $\beta$ (#152) models, though not the highest-symmetry one. This explains why it has sufficient freedom to fit both the $\alpha$- and $\beta$-phase data so well across the phase transition at 390 K, despite the structural differences between the two phases ($R_{wp} = 7.580$ and rank = 4 for $\alpha$; $R_{wp} = 4.180$ and rank = 5 for $\beta$).

We can see from Figure 7 that similar modes are important in each structure: large $\Gamma_5^-$ (shaded pink) and $L_2^1$ (yellow) Bi-modes and smaller $\Gamma_4^-$ (green) modes on all atoms. It is worth noting that for both structures the specific superposition of the appropriate $\Gamma_5^-$ and $L_2^1$ order parameters is primary (i.e., solely responsible for breaking the symmetry of the $\gamma$ parent). We can also see that the magnitudes of modes associated with the Bi$_2$O’ framework are much larger than those associated with SnO$_6$. This is reflected in the mean atomic displacements from ideal positions for the different atom types in the $\alpha$ ($\beta$)-structure of Bi 0.381 Å (0.355 Å), Sn 0.059 Å (0.041 Å), O 0.148 Å (0.118 Å), and O’ 0.253 Å (0.140 Å). The Bi displacement is similar to that found in PDF studies of disordered Bi$_2$Ti$_2$O$_7$.21

The effect of the large $\Gamma_5^-$ and $L_2^1$ modes is to cause rotations of the Bi$_4$O’ tetrahedra with minimal internal distortion of their bond distances and angles (Figure 8). In the undistorted parent structure the Bi$_2$O’ tetrahedra are close to regular: Bi−O’ distances are 2.315−2.317 Å and angles 108.9−109.8° (the ranges presented from here on encompass all crystallographically distinct coordination environments). With both $\Gamma_5^-$ and $L_2^1$ modes active, these ranges do not change greatly: 2.33−2.36 Å/108.7−110.6° for the $\alpha$ structure and 2.32−2.36...
where X modes describe the coupled rotations of rigid SiO$_4$/2 tetrahedra on changing from Fd$ar{3}$m to P4$_{1}$2$_{1}$2$_{1}$. The $\Gamma_{5}^{+}$ and $L_{2}$ modes give rise to tetrahedral rotations around different axes. Both the Aba2 $\beta$-phase and Cc $\alpha$-phase subgroup symmetries adopt the specific order parameter direction (OPD) $\Gamma_{5}^{+}$, which corresponds to a coupled

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<td>2.379(5)</td>
<td>2.408(5)</td>
<td>2.937(5)</td>
</tr>
<tr>
<td>Bi4</td>
<td>2.158(5)</td>
<td>2.384(5)</td>
<td>2.444(5)</td>
<td>2.952(5)</td>
</tr>
<tr>
<td>Sn1</td>
<td>2.018(6)</td>
<td>2.038(6)</td>
<td>2.042(6)</td>
<td>2.061(6)</td>
</tr>
<tr>
<td>Sn2</td>
<td>2.005(6)</td>
<td>2.022(6)</td>
<td>2.037(6)</td>
<td>2.044(6)</td>
</tr>
<tr>
<td>Sn3</td>
<td>2.027(6)</td>
<td>2.039(6)</td>
<td>2.068(6)</td>
<td>2.073(6)</td>
</tr>
<tr>
<td>Sn4</td>
<td>2.025(6)</td>
<td>2.046(6)</td>
<td>2.055(6)</td>
<td>2.063(6)</td>
</tr>
</tbody>
</table>
rotation of Bi$_4$O$_4$ tetrahedra around an axis parallel to $\langle 1\ 1\ 0 \rangle$ of the parent structure as shown in the top row of Figure 8. This causes Bi atoms to displace in the plane of their puckered hexagonal O coordination environment, moving toward a specific hexagon edge (the $96h$ site of the parent structure). The $\Gamma_5$ distortion corresponds to a $7.7^\circ$ rotation of tetrahedra around the $b$-axis of the $\alpha$-cell, and $60^\circ$ around the $a$-axis of the $\beta$-cell.

The effect of the four-mode $L_2^\alpha(a,b,c,d)$ order parameter is more complex, but the different OPDs it adopts are what distinguish the $\alpha$ - and $\beta$-structures. The difference is easy to visualize in the common subgroup #174 where the $\alpha$-structure adopts $L_2^\alpha(0,a,0,0)$ and the $\beta$-structure adopts $L_2^\beta(a,b,0,0)$ with $a = -b$. These $L_2^\alpha$ differences are also seen clearly in the bar chart of Figure 7, where the $a$ and $b$ branches of the $L_2^\alpha$ OPD have two modes of equal amplitude but opposite sign for the $\beta$-phase and only one mode for the $\alpha$-phase. The $L_2^\alpha(0,a,0,0)$ mode of $\alpha$-phase corresponds to an $8.2^\circ$ rotation of pairs of Bi$_4$O$_4$BiO$^-$Bi$_4$ tetrahedra around the parent $[1\ 1\ 1]$ axis with the Bi–O$^-$–Bi bond angle on the $[1\ 1\ 1]$ axis unchanged, but other Bi–O$^-$–Bi angles changing as shown in the lowest panel of Figure 8. The $L_2^\alpha(a,0,0,0)$ mode, which produces an equivalent rotation around $[1\ -1\ 1]$ axis, contributes to $\beta$ but not $\alpha$ (middle row of Figure 8), thus rotating one Bi$_4$O$_4$ tetrahedron by $10.5^\circ$ around the $c$-axis and the other by $7.5^\circ$ around the $a$-axis of the $\beta$-phase cell. The most significant difference between the two structures is the smaller $(1\ 1\ 1)$ rotation of the $\alpha$-phase.

The overall effect of the tilts on the local Bi coordination is shown in Figure 9. In the $\beta$-structure, the roughly equal amplitude $\Gamma_5$ and $L_2^\beta$ modes move four of the five Bi sites toward a hexagon edge and leave one (Bi4) unshifted. The result is that each Bi has two short (2.22–2.45 Å) and four longer (2.47–3.19 Å) bonds to O. The $\beta$-structure therefore has Bi environments similar to those proposed for disordered cubic Bi$_2$Ti$_2$O$_7$ phases. In the $\alpha$-structure the combined $\Gamma_5$ and $L_2^\alpha$ modes move Bi principally toward a hexagon vertex (only Bi4 moves precisely along the parent Bi–O vector), leading to three short (2.10–2.45 Å) and three longer Bi–O bonds (2.85–3.17 Å). The difference in the number of short Bi–O bonds (two for $\beta$ and three for $\alpha$) is accompanied by significantly different Bi$_4$O$_4$ framework distortions. In the $\beta$-structure, Bi–O$^-$ axial bonds in each Bi hexagonal bipyramid are reasonably symmetric (eight are 2.31 ± 0.01 Å; two are 2.45 Å). In the $\alpha$-structure, each Bi has one short (2.16–2.24 Å) Bi–O$^-$ bond and one longer Bi–O$^-$ (2.41–2.51 Å) bond. Overall, in the $\alpha$-structure the four Bi coordination environments are very similar, with five short bonds and three longer. In the $\beta$-structure the Bi environments are less uniform. Three are similar to $\alpha$ with five short and three longer bonds, whereas two (Bi4 and Bi5) lie on the 2-fold axis and have four short (2.3 Å), two intermediate (~2.7 Å), and two long (~2.9 Å) bonds.

### CONCLUSIONS

Symmetry modes provide a natural basis for both solving and describing structures that arise from phase transitions in complex functional materials. Here we demonstrate an automated and exhaustive symmetry-mode analysis of all possible superstructures derived from a parent phase, up to a maximum cell size that accommodates experimentally observed superlattice peaks and any other relevant evidence. The method provides a comprehensive, systematic, and straightforward comparison of different candidate models.
all 547 candidate structures that are consistent with previously reported models. Despite the subtlety and complexity of the distortions involved, we obtained unambiguous solutions to both the $\alpha$- and $\beta$-phase structures.

We describe the first reliable structure for $\beta$-Bi$_2$Sn$_2$O$_7$ with orthorhombic space group Aba2, and an $\alpha$-Bi$_2$Sn$_2$O$_7$ structure far simpler than previously reported, with monoclinic space group Cc. Relative to all other superstructural models, our solutions unambiguously optimize fits to the combined X-ray and neutron powder diffraction data sets with a minimum number of structural parameters.

The symmetry-mode parameterizations of the $\alpha$- and $\beta$-Bi$_2$Sn$_2$O$_7$ structures further illuminate their phase transitions in terms of rotations of the cristobalite-like Bi$_2$O$'$ framework, which displace Bi toward an edge of the O6 coordination hexagon in $\beta$ and toward an vertex in $\alpha$. These different distortions allow Bi to adopt the asymmetric coordination environment typical of a lone pair cation. Our exhaustive analysis leads us to believe that we now have definitive models for the known phases of this fascinating material.

The present combination of symmetry-mode analysis and exhaustive subgroup searching significantly expands the scope of structure determination in materials that exhibit complex symmetry-lowering phase transitions. These include fuel cells, Li-ion batteries and other vacancy or cation-ordered materials, metallic alloys, negative-thermal expansion materials, ferroelectrics, piezoelectrics, and other multiferroic systems, superconductors, and correlated-electron systems with competing lattice, charge, orbital, and magnetic degrees of freedom. Simple extensions of the present methods would include magnetic phase transitions, occupational orderings, whole-molecule reorientations, thermal vibrations, and polyhedral tilts.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04947.

Graph of $R_{wp}$ for three repeat exhaustive trials of all candidate models against $\alpha$- and $\beta$-phase data; multi-phase Rietveld fit of $\alpha$-Bi$_2$Sn$_2$O$_7$ X-ray data to show strain broadening; Rietveld fit to $\alpha$- and $\beta$-phase X-ray data using best candidate models, showing weak X-point distortions of the $\beta$-phase; histogram showing magnitude of displacive modes in $\alpha$-Bi$_2$Sn$_2$O$_7$; Rietveld fit of $\alpha$-Bi$_2$Sn$_2$O$_7$ X-ray data using Cc and Pc candidates; version of Figure 8 with parent $\gamma$-phase included; discussion of transformation of $\alpha$- and $\beta$-structures to their highest common subgroup; table listing all 547 candidate models; table showing the 30 lowest $R_{wp}$ candidates for the $\alpha$- and $\beta$-phases (PDF)

Crystalllographic information file of $\gamma$ parent structure (CIF)

Crystalllographic information file of $\alpha$-structure (CIF)

Crystalllographic information file of $\beta$-structure (CIF)

Crystalllographic information file of $\alpha$-structure in subgroup 174 setting (CIF)

Crystalllographic information file of $\beta$-structure in subgroup 174 setting (CIF)

ISODISTORT distortion file for the structure in subgroup 174 setting relative to the parent structure: alpha_st174-gamma_distortion (TXT)
Equivalent ISODISTORT distortion file for: beta_st174_domain17-gamma_distortion (TXT)
ISODISTORT distortion file for animated view of Figure 8 (left): bi2o_gamma_alpha_st174_bi4o_distortion (TXT)
ISODISTORT distortion file for animated view of Figure 8 (right): bi2o_gamma_beta_st174_domain17_distortion (TXT)

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