

Exhaustive symmetry mode searches: phase transitions in pyrochlore $\text{Bi}_2\text{Sn}_2\text{O}_7$ James William Lewis¹, Julia Payne¹, Ivana Evans¹, Harold Stokes², Branton Campbell², John Evans¹¹Department Of Chemistry, Durham University, Durham, United Kingdom, ²Department of Physics and Astronomy, Brigham Young University, Provo, United States
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$\text{Bi}_2\text{Sn}_2\text{O}_7$ pyrochlore has been shown to undergo phase transitions from a cubic parent γ phase to β and α phases on cooling. Until recently, the only reliable structural model for the low temperature phases has been an α phase model reported by Evans et al. [1]. This was derived by testing a limited number of candidate structures based on experimental information from the literature and assuming group-subgroup relationships.

We have now developed an exhaustive approach for searching all possible subgroups between a parent structure (here the γ phase) and a child structure with sufficient degrees of freedom to explain all the peaks seen in powder diffraction data from any form of the material (here a P1 structure with a cell parameters of $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, where a_p is the cell parameter of the parent cubic γ phase). Our method uses ISODISTORT [2] to produce a 547-membered subgroup tree and Topas Academic to automatically test each of the candidate structures. Using this approach we have determined the first definitive model for the β -phase (Aba2, $a = 7.571833(8)\text{\AA}$, $b = 21.41262(2)\text{\AA}$, $c = 15.132459(14)\text{\AA}$) and a much simpler model than previously reported for the α -phase (Cc, $a = 13.15493(6)\text{\AA}$, $b = 7.54118(4)\text{\AA}$, $c = 15.07672(7)\text{\AA}$, $\beta = 125.0120(3)^\circ$) [3].

By using a symmetry mode basis we can describe the principal distortions in each phase in terms of coupled rotations of the cristobalite-like $\text{Bi}_2\text{O}'$ framework that allow Bi to adopt lone-pair cation preferred low-symmetry sites. In the β -phase we find that Bi is displaced towards an edge of its O6 hexagonal coordination environment whereas in the α -phase the displacement is towards an apex.

The use of symmetry modes enables an exhaustive approach to symmetry determination in a modest time period (~48 hours on an i7, 3.4GHz desktop PC in this work) that is applicable across a range of structure determination problems where only powder diffraction data is available.

[1] Evans, I. R., Howard, J. A. K. and Evans, J. S. O. J. Mater. Chem. 2003, 13, 2098

[2] Campbell, B. J.; Stokes, H. T.; Tanner, D. E.; Hatch, D. M. Journal of Applied Crystallography 2006, 39, 607

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