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The structure of γ-$Bi_2Sn_2O_7$ at 725 °C by high-resolution neutron diffraction: implications for bismuth(III)-containing pyrochlores

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High-resolution neutron powder diffraction has been used to show that at 725 °C γ-$Bi_2Sn_2O_7$ does not adopt an ideal pyrochlore structure as was previously supposed. The bismuth(III) ion does not reside at a centre of symmetry ($\bar{3}m$) but is disordered on a site of lower symmetry. This results in a distortion of the co-ordination sphere of the Bi^{III}, in accord with the steric activity of the $6s^2$ lone pair. These results are compared with those for other known bismuth(III)-containing pyrochlores.

The pyrochlore structure is adopted by many binary metal oxides having the overall formula $A_2B_2O_7$.[1] In general, A is usually found in either oxidation state II or III, with the B cation in oxidation state V or IV respectively. It is also possible to produce defect materials and also ternary and higher mixed oxides with the pyrochlore structure. Compounds which have the pyrochlore structure have been investigated in a wide variety of technologically important contexts. These include their use as fast ion conductors,[2] catalysts for the oxidative coupling of methane[3,4] and the production of 'syn gas' (a mixture of CO and H_2),[5,6] electrocatalysts,[7] conducting components in thin-film resistors[8] and as selective gas-sensor materials.[9]

The space group of compounds which adopt the ideal pyrochlore structure type is $Fd\bar{3}m$. When the origin is at the centre of symmetry the A cations occupy the 16d sites and have coordinates $x = y = z = 0.0$. The B cations occupy the 16c site with $x = y = z = 0.5$. There are two crystallographically distinct oxygen sites, the 8d site with $x = y = z = 1/8$ and the 48f site with coordinates, x, 0.0, 0.0. Thus there is only one positional parameter, the x coordinate of the 48f oxygen.

The pyrochlore structure itself can be described in a variety of ways, for example derived from a defect fluorite cell,[10] or built up from two interpenetrating networks.[11,12] The co-ordination of the B cation which occupies the 16c site can vary between trigonal antiprismatic and octahedral, whilst that of the A cation occupying the 16d site can vary between cubic and a distorted arrangement with six oxygen atoms surrounding the bismuth atom in a puckered hexagonal arrangement with two shorter $A \cdots O$ interactions at right angles to the plane of the hexagon of oxygens. The precise co-ordination of the B site is determined by the value of the x coordinate of the 48f oxygen. The closer is its value to 0.4375 the closer is the co-ordination to ideal octahedral. It should be noted that both of the metal sites are at a centre of symmetry in space group $Fd\bar{3}m$. This however raises problems when one of the cations itself possesses a stereochemically active lone pair of electrons which will tend to move the cation from this site to one of a lower symmetry with a lowering of the symmetry of the structure. Such behaviour is often thought to be responsible for the ferroelectric properties associated with these materials when the symmetry lowering results in a polar space group.

A pyrochlore which has recently been studied in a variety of contexts is bismuth stannate, $Bi_2Sn_2O_7$. It has found uses as a material in gas-sensing devices[9] and the bismuth-rich phase $Bi_2Sn_{2-x}Bi_xO_{7-2x}$ ($0 \leqslant x \leqslant 0.86$) is an effective catalyst for the oxidative coupling of methane.[4] Despite its apparent simplicity the crystal chemistry of $Bi_2Sn_2O_7$ is not well understood. This is believed to be the result of the steric activity of the lone pair of electrons on the bismuth(III) ion. At room temperature $Bi_2Sn_2O_7$ exhibits second harmonic generation indicating a non-centrosymmetric space group, however attempts to measure the dielectric hysteresis curve were unsuccessful.[13] As a result of the lone pair this material undergoes a series of phase transitions which are accompanied by a loss of second harmonic generation until at 690 °C the γ phase is reached which was thought to adopt an ideal pyrochlore structure.[13] In this paper we show this phase is in fact a distorted pyrochlore phase. We were able to do this by collecting neutron diffraction data to low d spacings (≈0.63 Å) which enabled us successfully to refine the structure in a disordered model.

Experimental

The compound $Bi_2Sn_2O_7$ was prepared by a literature method[13] except that a gold boat instead of a platinum crucible was used to contain the pellets of the mixed precursor oxides. The purity of the sample was confirmed by powder X-ray diffraction using a laboratory diffractometer.

The sample was lightly packed into a 11 mm diameter cylindrical vanadium can mounted on the centre stick of the furnace and a chromel–alumel thermocouple was tied with tantalum wire to the sample can. The end of the thermocouple was approximately 3 mm from the top of the neutron beam and 13 mm from the beam centre. The centre stick was loaded into the furnace and the entire volume of the furnace was evacuated to 10^{-4} mbar (bar = 101 325 Pa) before heating to 725 °C.

Data were collected for 7 h on the high-resolution powder diffractometer at the ISIS neutron spallation source. Data were collected in time-of-flight mode in time channel bins (interval t_1 to t_2) of $\Delta t/t = 1 \times 10^{-4}$ from 30 to 230 ms which corresponded to a d-spacing range of 0.6 to 4.6 Å in the high-resolution back-scattering detector bank. The data were focused, background subtracted, normalised to the incident flux distribution using an upstream monitor, corrected for detector efficiency using a spline-fitted diffraction pattern from a vanadium standard and finally rebinned from 31 to 190 ms in time channel bins of $\Delta t/t = 3 \times 10^{-4}$ for profile refinement.[14]

The pattern was subjected to a model-independent fit using the CAILS[15] routine of the time-of-flight Rietveld program TF12LS,[16] in the space group $Fd\bar{3}m$ (no. 227). This yielded the values for the profile parameters (peaks widths, lattice parameter and background) with residuals of $R_p = 0.0356$, $R_{wp} = 0.0323$, $\chi^2 = 1.796$. These were then used subsequently as starting values for a full Rietveld refinement.[17,18] In an ideal pyrochlore structure there is only one atomic positional parameter that can be varied, *i.e.* the x coordinate of the 48f oxygen atom.

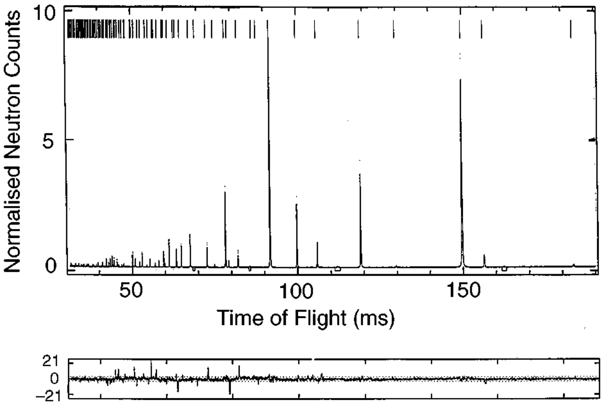

Fig. 1 Observed (·), calculated (continuous line) and difference plots ÷ estimated standard deviation (e.s.d.) for the ideal pyrochlore model from 31 to 190 ms (d spacing ≈0.64 to 3.94 Å)

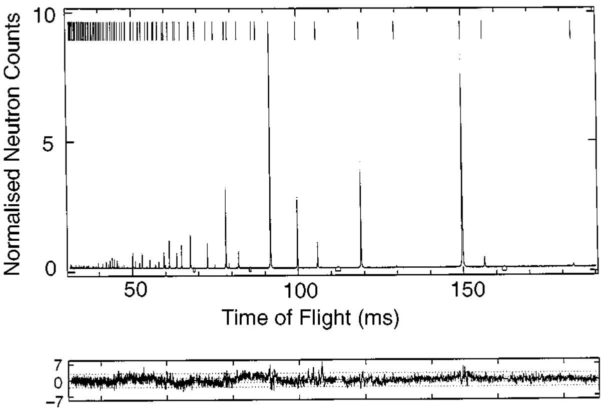

Fig. 2 Observed (·), calculated (continuous line) and difference plots ÷ e.s.d. for model 1 from 31 to 190 ms (d spacing ≈0.64 to 3.94 Å)

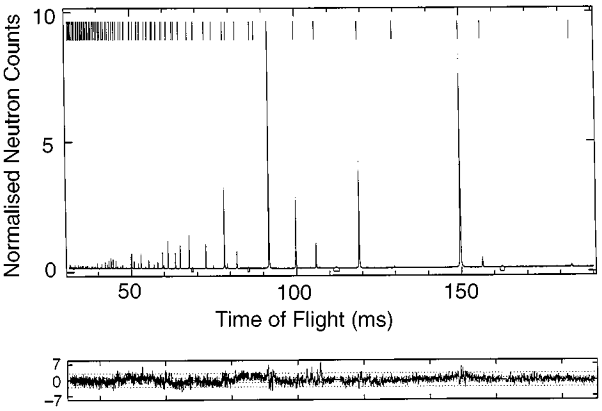

Fig. 3 Observed (·), calculated (continuous line) and difference plots ÷ e.s.d. for model 2 from 31 to 190 ms (d spacing ≈0.64 to 3.94 Å)

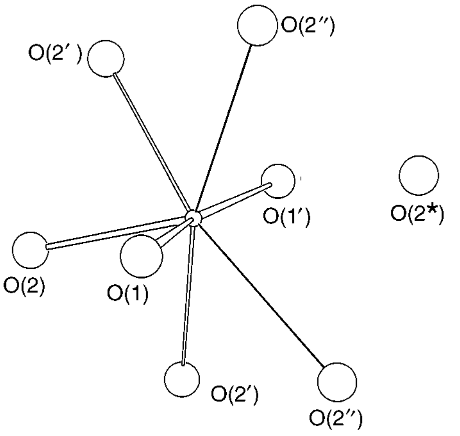

Fig. 4 Co-ordination around Bi for model 1. Thick lines (unshaded) represent short contacts <2.37 Å, thin lines (unshaded) intermediate contacts of 2.51 Å and thin lines (shaded) contacts of 2.86 Å

Initial starting values for the positional parameters of the ions were taken from those of $La_2Sn_2O_7$.[19] Inclusion of isotropic thermal parameters and the one variable positional parameter quickly converged to $R_p = 0.0484$, $R_{wp} = 0.0687$, $\chi^2 = 5.843$. It was then decided to let O(2) vibrate anisotropically, producing the residuals $R_p = 0.0436$, $R_{wp} = 0.0583$, $\chi^2 = 4.743$. Plots of the observed, calculated and difference values are given in Fig. 1. It can be clearly seen that there are large discrepancies at low d spacing (short times of flight) implying that there are difficulties in the proposed model. Another feature of the model which seemed implausible was that B_{iso} for the bismuth ion was 6.17 Å^2 compared with a value of 1.08 Å^2 for the tin ion. This large discrepancy seemed much greater than could be simply accounted for because of the larger free volume available for the Bi to vibrate in. Other models were tried, including the placement of oxygen interstitials and disorder of the cation sublattice, but in none of the models was there any substantial improvement of the fit. Finally it was decided to disorder the location of the bismuth ion by reducing the symmetry of the site it occupies from $\bar{3}m$ to m (96g), and changing the occupancy to preserve stoichiometry. This model converged smoothly to give residuals of $R_p = 0.0353$, $R_{wp} = 0.0373$, $\chi^2 = 1.941$, in excellent agreement with the model-independent fit suggesting that this model (model 1) is substantially correct. A fit of the observed and calculated and difference diffraction profiles for model 1 is shown in Fig. 2. Unfortunately it is also proved possible to produce a satisfactory refinement with the bismuth ion disordered to a site of two-fold symmetry (96h) and giving residuals of $R_p = 0.0354$, $R_{wp} = 0.374$, $\chi^2 = 1.952$ (model 2); a fit of the observed and calculated and difference diffraction profiles is shown in Fig. 3. The thermal parameter of Bi(1) was thus reduced from 6.2 to 1.71 (model 1) and 1.73 Å^2 (model 2). In both of these models there is one slightly worrying feature, *vis-à-vis* the thermal parameter of O(1) which is relatively large. Attempts further to improve both models by displacing this oxygen atom with coordinates $x = y = z = 1/8$ off this special position did improve the fit, $R_p = 0.0354$, $R_{wp} = 0.0373$, $\chi^2 = 1.944$ (Bi at 96g site, model 3) and $R_p = 0.0354$, $R_{wp} = 0.0373$, $\chi^2 = 1.946$ (Bi at 96h site, model 4). In both cases there was a reduction in the thermal parameter of this atom. Since however both refinements with the displaced oxygen parameter depended crucially upon the starting value of the O(2) x coordinate and there was only a marginal reduction in the residuals, it is difficult to justify this extra complication to the model on statistical grounds, and hence we retained models 1 and 2. However the large thermal parameter for this oxygen atom may indicate that the oxygen atom which is at site of cubic symmetry ($\bar{4}3m$) is in fact vibrating anharmonically and that the harmonic approximation is incorrect. This feature has long been known in materials of high symmetry, *e.g.* CaF_2.[20] Alternatively it may be that the oxygen atom is genuinely displaced so as to give rise to a shorter contact with the bismuth ion.

Table 1 lists crystallographic data for γ-$Bi_2Sn_2O_7$, Table 2 lists atomic parameters for both models 1 and 2 and selected interatomic contacts and angles for these models are given in Tables 3 and 4.

Discussion

The tin atom is surrounded by six oxygen atoms in approximately octahedral co-ordination as indicated by the value of the x coordinate (0.4242) of the 48f oxygen atom. The Sn–O contacts are in good agreement with those observed in several lanthanide stannates $Ln_2Sn_2O_7$[19] (Ln = La, 2.070; Sm, 2.054; Y, 2.048 Å) and other compounds with tin in octahedral co-ordination, *e.g.* in the rutile form of SnO_2[21] (2.052 and 2.056 Å) and in the perovskite $BaSnO_3$[22] (2.058 Å). The most interesting feature of the structure is the co-ordination of the bismuth ion. In both models the lone pair is sterically active. This whilst unusual at this elevated temperature is not unprecedented as it has been observed in Bi_2WO_6[23] at temperatures up to 950 °C. This results in a displacement of the Bi away from the centre of symmetry. In both cases the lone pair of electrons is directed towards a vacant site in the bismuth co-ordination polyhedron which has been explained theoretically by mixing of the s and p orbitals on the metal ion.[24] It is not possible to distinguish between the two possible models on the grounds of chemical plausibility as both are reasonable and merit some discussion.

The co-ordination around the bismuth for model 1 is shown in Fig. 4. The Bi atom makes three short Bi–O contacts of less than 2.37 Å, two intermediate contacts of 2.51 Å, two longer contacts of 2.86 Å and one very long contact of 3.0 Å. If we consider the five shortest contacts the Bi atom can be considered to be in extremely distorted octahedral co-ordination with one of the vertices missing. The longest contact of 3.1 Å can be placed at the missing vertex of the octahedron, with the two other Bi–O contacts positioned about the line linking the Bi atom with the most distant oxygen. The co-ordination can be most easily derived from the pseudo-cubic co-ordination of the bismuth ion in an ideal pyrochlore structure by distorting the structure by removing three of the oxygen atoms from one of the faces of the cube. The longest Bi–O contact is *trans* to the shortest Bi–O distance whilst the two long Bi–O contacts of 2.8 Å are *trans* to the intermediate Bi–O contacts of 2.5 Å. The overall effect is to produce a vacant site in the immediate bismuth co-ordination sphere along which the bismuth $6s^2$ lone pair is presumably oriented. This structure is similar to that seen in other bismuth compounds, *e.g.* in α-Bi_2O_3[25,26] or in the sillenite phases such as $Bi_{12}SiO_{20}$[27] or $Bi_{12}TiO_{20}$.[28]

Table 1 Crystallographic and experimental details for γ-$Bi_2Sn_2O_7$

Space group	$Fd\bar{3}m$
Lattice parameter a/Å	10.7435(1)
Number of data points	5923
Number of contributing reflections	145
Number of excluded regions	4
Number of refined parameters	
(model 1)	10
(model 2)	9

The co-ordination around the bismuth ion when two-fold symmetry is retained (model 2) is somewhat different and is illustrated in Fig. 5. It most closely resembles that of β-Bi_2O_3[29] where the structure was described as being based on a pseudo-trigonal bipyramid with the lone pairs occupying an equatorial site. In model 2 there are four short contacts of 2.353–2.369 Å which could be thought to constitute the pseudo-trigonal bipyramid. However the equatorial angle is much more compressed at 72.1° compared to that seen in β-Bi_2O_3 (121°). There are two longer Bi–O contacts of 2.690 Å and if these constitute the co-ordination sphere of Bi then the geometry is now best described as a pseudo-pentagonal bipyramid with the lone pair once again lying in the equatorial plane. The co-ordination around the Bi can again be easily derived from the 6 + 2 co-ordination seen in an ideal pyrochlore. If we consider that the two oxygen atoms are removed from an edge of the pseudo-cube around the Bi this creates the pseudo-pentagonal bipyramid with the lone pair lying in the equatorial plane.

Since we had substantially improved our fit by displacing the bismuth ion off the centre of symmetry we examined the ICSD data base[30] to see if this had been previously reported in any other bismuth-containing pyrochlores. The six structures where both the thermal parameters of the Bi and B cation had been refined independently all showed this feature. These results are

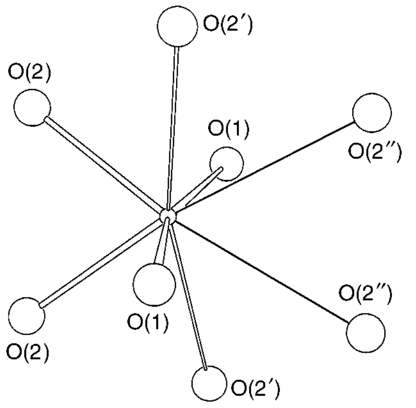

Fig. 5 Co-ordination around Bi for model 2. Thick lines (unshaded) represent short contacts <2.37 Å, thick lines (unshaded) intermediate contacts of 2.69 Å and thin lines longest contacts of 2.98 Å

Table 2 Fractional atomic coordinates and thermal parameters with e.s.d.s in parentheses

(*a*) Model 1

Atom	x	y	z	B_{iso} or B_{eq}/Å^2
Bi	0.0128(5)	0.0128(5)	−0.0279(5)	1.71(4)
Sn	0.5	0.5	0.5	1.24(2)
O(1)	0.125	0.125	0.125	4.39(5)
O(2)	0.4242(1)	0.125	0.125	2.52(3)

Anisotropic thermal parameters

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(2)	2.42(3)	2.57(2)	2.57(2)	0.0	0.0	−1.40(2)

(*b*) Model 2

Atom	x	y	z	B_{iso} or B_{eq}/Å^2
Bi	0.0	0.0235(1)	−0.0235(1)	1.73(4)
Sn	0.5	0.5	0.5	1.24(2)
O(1)	0.125	0.125	0.125	4.40(5)
O(2)	0.4242(1)	0.125	0.125	2.55(3)

Anisotropic thermal parameters

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(2)	2.50(3)	2.57(2)	2.57(2)	0.0	0.0	−1.40(2)

Table 3 Interatomic contacts (Å) and angles (°) with e.s.d.s in parentheses for model 1

Sn–O(2) × 6	2.0664(4)	Bi–O(2′) × 2	2.507(5)
Bi–O(1)	2.368(5)	Bi–O(2″) × 2	2.862(5)
Bi–O(1′)	2.339(5)	Bi–O(2*) × 1	3.016(5)
Bi–O(2)	2.318(5)		
O(2)–Sn–O(2) × 6	84.84(3)	O(2″)–Bi–O(2″)	105.2(2)
O(2)–Sn–O(2) × 6	95.16(3)	O(2)–Bi–O(2″) × 2	122.3(2)
O(2)–Sn–O(2) × 3	179.97(3)	O(2′)–Bi–O(2′)	130.0(2)
O(1)–Bi–O(1′)	162.5(3)	O(2′)–Bi–O(2*) × 2	110.4(2)
O(1)–Bi–O(2″) × 2	75.2(1)	O(2)–Bi–O(2′) × 2	70.5(1)
O(1)–Bi–O(2′) × 2	103.7(2)	O(2)–Bi–O(2*)	176.6(2)
O(1)–Bi–O(2*)	90.0(2)	O(1′)–Bi–O(2″) × 2	94.5(2)
O(1)–Bi–O(2)	86.6(2)	O(1′)–Bi–O(2′) × 2	83.0(2)
O(2′)–Bi–O(2″) × 2	62.2(1)	O(1′)–Bi–O(2*)	72.5(1)
O(2′)–Bi–O(2″) × 2	166.7(2)	O(1′)–Bi–O(2)	110.9(2)
O(2″)–Bi–O(2*) × 2	56.6(1)		

The designations O(1′), O(2′), O(2″) and O(2*) refer to symmetry-related atoms as illustrated in Fig. 4.

summarised in Table 5. Indeed one set of authors commented on this feature and concluded that it was probably the result of the anharmonicity of the vibration of the bismuth ion as their attempts to move this ion off a centre failed.[31] Thus it is possible that structures in which the Bi has been reported as lying at the centre of symmetry (16d site) are only partially correct and that they may be more accurately described as disordered structures. This would be in accord with the observation that $Bi_2Sn_2O_7$ itself and several other Bi-containing pyrochlores are found at room temperature in distorted pyrochlore structures. This has not unnaturally been attributed to the steric activity of the lone pair of the bismuth ions. If we relate the symmetry lowering in $Bi_2Sn_2O_7$ to the presence of the lone pair it thus appears that in $Bi_2Sn_2O_7$ itself the steric activity of the lone pair persists in the centrosymmetric phase. Ferroelectricity has been observed in a number of bismuth-based compounds and related to the effect of the lone pair, but Shannon *et al.*[13] could not measure a dielectric hysteresis loop using single crystals of $Bi_2Sn_2O_7$ at room temperature; a positive result would indicate that the space group was not only non-centrosymmetric but also polar. The failure to measure the hysteresis loop may be because the compound is indeed non-polar at room temperature but it could also arise from the presence of multiple ferroelastic domains that were present in these crystals which they could not eliminate. As the crystal structure of the room-temperature phase is unknown an attempt to measure the hysteresis loop on a monodomain crystal would prove important for space group determination.

Conclusion

Despite our inability firmly to conclude whether the co-ordination around the bismuth ion is best described as pseudo-octahedral or pentagonal trigonal bipyramidal, we have shown clearly that the bismuth ion is displaced away from a centre of symmetry by the substantial improvements in our refinements when this is taken into account. This had the effect of bringing the thermal parameter of the bismuth more into line with those of the other atoms in the structure from its unreasonably high value. Examination of the literature has shown that for most accurate structures of Bi^{III}-containing pyrochlores the same feature had been reported as we had observed at an intermediate stage during our refinement, *i.e.* anomalously high thermal parameters for Bi. We believe that in these structures the bismuth(III) ion may also not reside at a centre of symmetry but in fact is at a site of lower symmetry. This seems reasonable in the light of the heavier metallic elements of the p block in their lower oxidation states, Tl^{I}, Pb^{II} and Bi^{III} which adopt structures in which the steric activity of the $6s^2$ lone pair of electrons is pronounced. In order to conclude which of the two models is correct it will be necessary either to carry out a high-temperature extended X-ray absorption fine structure experiment in order to probe the local arrangement of atoms around the bismuth or a high-temperature single-crystal neutron diffraction study.

Table 4 Interatomic contacts (Å) and angles (°) with e.s.d.s in parenthesis for model 2

Sn–O(2) × 6	2.0664(4)	Bi–O(2′) × 2	2.690(1)
Bi–O(1) × 2	2.355(1)	Bi–O(2″) × 2	2.977(1)
Bi–O(2) × 2	2.369(1)		
O(2)–Sn–O(2) × 6	84.84(3)	O(2)–Bi–O(2)	72.08(3)
O(2)–Sn–O(2) × 6	95.16(3)	O(2)–Bi–O(2′) × 2	66.52(2)
O(2)–Sn–O(2) × 3	179.97(3)	O(2)–Bi–O(2′) × 2	127.81(4)
O(1)–Bi–O(1)	162.55(5)	O(2)–Bi–O(2″) × 2	116.04(1)
O(1)–Bi–O(2) × 2	85.79(3)	O(2)–Bi–O(2″) × 2	171.89(3)
O(1)–Bi–O(2) × 2	108.59(5)	O(2′)–Bi–O(2′)	164.75(5)
O(1)–Bi–O(2′) × 2	78.88(3)	O(2′)–Bi–O(2″) × 2	58.68(2)
O(1)–Bi–O(2′) × 2	98.78(2)	O(2′)–Bi–O(2″) × 2	106.57(4)
O(1)–Bi–O(2″) × 2	91.26(4)	O(2″)–Bi–O(2″)	55.85(2)
O(1)–Bi–O(2″) × 2	73.13(3)		

The designations O(2′) and O(2″) refer to symmetry-related atoms as illustrated in Fig. 5.

Table 5 Thermal parameters for selected bismuth pyrochlores

	B_{iso}/Å^2		
Compound	Bi	B cation	Ref.
$Bi_2Sn_2O_7$	6.2	1.1	This work, refined as ideal pyrochlore
$CsBi_2Ta_5O_{16}$	5.3	0.52	31
$CsBi_2Nb_5O_{16}$	6.1	0.89	31
$RbBi_2Ta_5O_{16}$	4.9	0.45	31
$Bi_2Rh_2O_{6.8}$	0.7	0.1	32
$Bi_2Pt_2O_7$	1.9	0.8	33
$Bi_2Ru_2O_7$	0.9	0.1	34

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