instead of two times, larger than those of Cu₄O, which indicates that the expansion of the Cu₄O lattice due to the interstitial O atoms in the Cu lattice is less than that in Cu₆O. It is possible that such a strain may cause distortions of the substrate metal and if the strain is large enough it will result in a separation of the ‘oxidized’ part from the matrix and produce a large number of very small and thin slightly ‘oxidized’ crystallites. This may be one of the reasons why Cu₆O can be more easily found than Cu₄₄O during observation in the electron microscope. It may be noted that, for the suboxides with very low oxygen content, the structure images cannot be obtained from a very thin crystal, i.e. the weak phase object condition, but can be obtained from a thicker specimen in the dynamic scattering object condition. On increasing the thickness of the crystal to more than a certain critical thickness, the contrast of the images of the heavy atoms decreases and that of the light atoms increases. Thus at some optimum thickness of the crystal, the images of the light atoms can be observed as well as those of the heavy atoms. Thus the dynamical scattering of electron waves can be used effectively for the structure analysis of the crystals containing light atoms.

The authors would like to record their thanks to Mr B. S. Zou and Drs H. Endoh, M. Tomita and N. Ajika for their help in the experiments and to Mr Y. K. Wu, and Professors G. Thomas and S. Suryanarayana for helpful discussions.

References


A Combined X-ray and Neutron Diffraction Study of Bi₃ReO₈; a New Structure Type Based on Fluorite

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Abstract

The fluorite-related crystal structure of Bi₃ReO₈ has been solved by a combination of X-ray and neutron diffraction techniques. The lattice is cubic, a = 11.590 (1) Å, space group P2₁3, Z = 8. The final R factors from the neutron powder study were Rᵢ = 5.3%, R_p = 10.4%. The principal deviation from the ideal fluorite structure is found in the ReO₄ tetrahedra, which are rotated 40° about the ⟨111⟩ direction in order to accommodate the stereochemical activity of the Bi lone pairs. The relationship of the structure to those of the related rare-earth compounds, Ln₃ReO₈, is discussed.

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A COMBINED X-RAY AND NEUTRON DIFFRACTION STUDY OF Bi$_3$ReO$_8$

Introduction

We have described the preparation and characterization of Bi$_3$ReO$_8$ in previous papers on our investigation of the Bi–Re–O system (Cheetham & Rae Smith, 1981; Rae Smith & Cheetham, 1979). It is the most stable compound in the Bi$_2$O$_3$–Re$_2$O$_7$ system, possessing no appreciable range of composition and melting above 1473 K, and is the sole product obtained when phases containing more than 25% Re$_2$O$_7$ are heated in air above 873 K. Colourless crystals may be grown by vapour transport at 1073 K from reaction mixtures of ReO$_3$ and Bi$_2$O$_3$ (the other major product being BiRe$_2$O$_6$). The polycrystalline material has a very pale cream colour.

In this paper we describe the determination of the crystal structure. The space group and metal-atom positions were derived from a combination of single-crystal and powder X-ray diffraction data, but because of the high pseudosymmetry of the metal-atom positions, the O atoms could not be located. A powder neutron diffraction study allowed a choice to be made between the various models, leading to the complete determination of the structure.

Experimental

The X-ray powder diffraction data were collected on a Philips X-ray powder diffractometer using Cu Kα radiation. The diffracted intensity was measured to a 2θ limit of 85° with a step size of 0.01°. A high monitor count was used to ensure good statistics for the weak superlattice reflections. The data yielded a total of 72 resolved peaks corresponding to 186 independent reflections.

The X-ray single-crystal data were collected on an Enraf–Nonius CAD-4F diffractometer using Mo Kα radiation. Intensities of 2345 reflections were collected to a 0 limit of 30°. After applying Lorentz and polarization corrections, equivalent reflections were merged to yield 433 reflections with $I/\sigma(I) > 2$. The crystal was small (average diameter 0.1 mm) and multi-faceted, with the prominent {110} faces giving the crystal a rhombic dodecahedral appearance. This made the application of the necessary absorption correction (de Meulenaer & Tompa, 1965) ($\mu = 910$ cm$^{-1}$) extremely difficult, and attempts to do so were unsatisfactory.

The neutron powder data were collected on the DIA high-resolution powder diffractometer at the ILL, Grenoble. The diffracted intensity was measured to a 2θ limit of 150° with a step size of 0.05°, using a neutron wavelength of 1.511 Å. The sample (8 g of polycrystalline Bi$_3$ReO$_8$) was contained in a vanadium can.

X-ray calculations were carried out using the Oxford CRYSTALS package (Carruthers, 1978) for the single-crystal data and a local program (Wiseman, 1974) for the analysis of powder intensity data. Calculations on the neutron powder data used an interactive version of the Rietveld profile refinement program (Rae Smith, Cheetham & Skarnulis, 1979). All values for X-ray scattering factors and anomalous-dispersion coefficients were taken from International Tables for X-ray Crystallography (1974). Values of 9.2, 8.6 and 5.8 fm were taken for the neutron scattering lengths of Re, Bi and O respectively.

Determination of the structure

Determination of the space group

The X-ray diffraction data showed that the lattice was cubic, with cell parameter $a = 11.590$ (1) Å, and the intensity distribution indicated a relationship to the fluorite structure with $a = 2a_F$, where $a_F$ is the cell parameter of the face-centred fluorite subcell. For convenience we shall refer to those reflections indexable on the fluorite subcell $(h/2, k/2, l/2$ all even or all odd) as sublattice reflections, and the remaining weaker reflections as superlattice reflections. The ratio of the X-ray intensities of the strongest sublattice to the most intense superlattice reflection is 15:1.

The X-ray single-crystal data indicated that the Laue group was $m\overline{3}$ ($I_{hkl} \neq I_{hkl}$) rather than $m\overline{3}m$ and suggested the systematic absence condition $h00$, $h = 2n + 1$. However, this class of reflections is very small and falls exclusively among the weaker superlattice reflections, and so we could not discount the possibility that these absences were accidental. An additional feature of the data is that all the stronger superlattice reflections obey the condition $h + k + l = 2n$, implying that the large cell is approximately body-centred.

Examination of the infrared spectrum of Bi$_3$ReO$_8$ narrowed down the choice of space groups. The spectrum (see Fig. 1) shows intense peaks around $1000$ 800 600 400 cm$^{-1}$...
900 cm\(^{-1}\), characteristic of tetrahedrally coordinated Re\(^{VII}\) as found in the perrhenates (Busey & Keller, 1964; Ulbricht & Kreigsmann, 1968) and illustrated in Fig. 1 by the spectrum of Bi(ReO\(_4\)). These peaks are absent in compounds such as L\(_3\)ReO\(_4\) that contain octahedrally coordinated Re\(^{VII}\). The presence of approximately tetrahedral ReO\(_4\) units in an ordered structure limits the point group to 23 and the space groups to P2\(_{3}\) and P2\(_{1}3\), with the body-centred groups 123 and I2\(_{3}\) giving close approximations. The systematic absence condition favours P2\(_{3}\), but for the reasons described above, P2\(_{3}\) must also be taken into consideration.

### Determination of the metal-atom positions

Preliminary calculations using the X-ray powder data indicated that the metal-atom positions were slightly displaced from the ideal fluorite positions, since merely ordering the Re and Bi atoms on the metal sites did not generate sufficient superlattice intensity. The calculations also showed that the required displacements were quite small (<0.35 Å).

Three types of Patterson function were calculated from the single-crystal data: a standard Patterson function employing all reflections, a sharpened Patterson function, and a Patterson function based on the superlattice reflections alone. The small values of the displacements combined with the high lattice symmetry resulted in broad metal–metal vectors in the Patterson functions, and made it impossible to deduce anything about the ordering of the atoms or the nature of the displacements. Direct methods were also tried, but met with no success. This is doubtless due to the high lattice symmetry and the pseudosymmetry of the metal-atom positions, together with the noncentrosymmetric nature of the structure.

The positions of the symmetry elements in the space groups P2\(_{3}\) and P2\(_{1}3\) lead in each case to four possible models for ordering the metal atoms. The ideal positions for these models may be derived by placing the Re atoms on the body diagonal of the large cubic cell at positions (0, 0, 0), (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)), (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)) or (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)), and on the body-centred related positions. These we shall term models (1)–(4), respectively, in each space group. The Re positions are fourfold (x, x, x) positions except for model P2\(_{3}\)-(1) which contains a combination of two invariant sites for the Re atom: (0, 0, 0) and the threefold position (\(\frac{1}{2}, 0, 0\)). The Bi atoms occupy the remaining sites in the face-centred array. These models are illustrated in Fig. 2. The metal ordering in models (1) and (2) can be described in terms of the fluorite subcell as that found in Cu\(_3\)Au and other alloys, while the metal ordering in models (3) and (4) requires a description in terms of the larger cell. Models P2\(_{3}\)-(3) and P2\(_{3}\)-(4) have the chemically unsatisfactory feature of Re\(_4\)O coordination clusters.

Table 1. Summary of X-ray refinements of metal-atom positions

<table>
<thead>
<tr>
<th>Model</th>
<th>R factors (R(_F)) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>P2(_{3})</td>
<td>16-1</td>
</tr>
<tr>
<td>P2(_{1}3)</td>
<td>16-4</td>
</tr>
</tbody>
</table>

Metal-atom positions [model P2\(_{3}\),(3)] used as starting positions in neutron calculations

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(1)</td>
<td>0-108</td>
<td>0-108</td>
</tr>
<tr>
<td>Re(2)</td>
<td>0-602</td>
<td>0-602</td>
</tr>
<tr>
<td>Bi(1)</td>
<td>0-095</td>
<td>0-365</td>
</tr>
<tr>
<td>Bi(2)</td>
<td>0-133</td>
<td>0-112</td>
</tr>
</tbody>
</table>

We then resorted to trial-and-error methods. For each model, the metal atoms were displaced from their ideal positions and the atomic positional coordinates refined. The initial displacements were varied until a set was found that converged to a minimum in less than four cycles of refinement. The powder data proved more stable in refinement using this technique, and were used to obtain the optimum displacements in each of the eight models. These values were then refined together with individual anisotropic thermal parameters using the single-crystal data. The final R factors (based on structure factors, R\(_F\) = \(\sum |F_o| - |F_c|/\sum |F_o|\)) are shown in Table 1. Disappointingly, there is no great preference for any one model, although P2\(_{3}\)-(3) and P2\(_{3}\)-(2) have the lowest values. Examination of the data showed that they suffered severely from extinction and absorption. While the complex shape of the crystal led to a lack of success in correcting for absorption, application of an extinction correction lowered the R factors by 3% from the values shown in Table 1.

Because of the high pseudosymmetry of the metal-atom positions, it was important to establish that the models had not refined to false minima. To examine this possibility, a series of R-factor maps was calculated for each model. Each positional parameter was allowed to vary in nine steps with initial bounds of ±0-08 from the ideal position. The step size was decreased when minima were found. The R factor decreased when minima were found.
A COMBINED X-RAY AND NEUTRON DIFFRACTION STUDY OF Bi₃ReO₈

was calculated from 80 reflections using the powder intensity data, and a Fortran program was written to minimize the calculation involved. A typical computation time for $4 \times 10^5$ $R$ factors varying all 8 parameters was 120 s on a CDC 7600 computer. The results of these calculations confirmed that the positions found by trial and error were in fact the lowest minima in each map.

**Determination of the O-atom positions**

Difference Fourier calculations based on the eight models for the metal-atom positions failed to reveal any O-atom positions that were both acceptable and stable on refinement, but a re-examination of the Patterson maps revealed a small but distinct peak at $(0, -0.064, 0.139)$ in maps derived from powder as well as single-crystal data. This peak is at a distance of 1.77 Å from the origin and has the correct height for a Re-O vector (55 based on an origin peak of 999). Although it is unusual to see metal-O vectors in Patterson functions of structures containing such large heavy-metal atoms ($Z_{\text{Re}} = 75$, $Z_{\text{Bi}} = 83$), the vector length is typical of that found in compounds containing tetrahedral ReO₄ groups. Moreover, it makes an angle of 106.4° (approximately tetrahedral) with the [111] direction. It is considerably displaced from the vector that would be observed if the O atom was simply drawn towards Re from the ideal fluorite position in order to make a sensible Re-O bond length $(0.088, 0.088, 0.088)$. The displacement corresponds to a rotation of 40° about the [111] direction.

O tetrahedra were then placed around the Re positions in each model, using the vector found in the Patterson map and placing the fourth O of each tetrahedron on the threefold axis. However, the O positions were not stable on refinement in any of the models, nor did they help to reveal any remaining O-atom positions in difference Fourier maps. While this situation was unsatisfactory, it was not totally unexpected. If the major distortion of the structure occurs in the O sublattice (as is apparent from the large rotation of the ReO₄ tetrahedra), the relative contribution of the O atoms to the superlattice reflections is much greater than that expected from a consideration of the relative scattering lengths of Bi, Re and O. Thus unless the O-atom positions are known with reasonable precision, the Fourier functions will not be phased correctly. We therefore attempted to solve the structure from neutron powder diffraction data, since with neutron radiation the O atoms represent the major scattering material in the unit cell, having a contribution of 57% compared to the corresponding value of 16% for X-rays.

Two points emerge immediately from a comparison of the X-ray and neutron powder scans (Fig. 3). First, the deduction made above, that the major distortion is in the O sublattice, is clearly justified, since the intensity ratio of the most intense sublattice to the most intense superlattice reflection is now 2:1 compared to the X-ray value of 15:1. Second, the approximate body-centring of the large cell is even more apparent in the neutron data, allowing preliminary calculations to be carried out in the body-centred space groups.

The $R$-factor-map technique described above was used to identify suitable starting positions for the O atoms in later refinement: 41 intensities, corresponding to 79 reflections, were used in these calculations. The metal atoms were placed in the positions determined from the X-ray analyses and the O atoms in the ReO₄ tetrahedra were placed on the positions derived from the X-ray Patterson vector. This left half of the O-atom positions to be found. The number of parameters was limited to four in most cases by carrying out the calculations in the body-centred space group. This allowed a larger range of positions for the O atoms to be searched. The displacements were centred about ideal fluorite positions.

Two models, $P_{213-(1)}$ and $P_{213-(3)}$, gave sets of positions with $R$ factors of less than 25%, and these were then used in the profile refinement. Initially, refinement was carried out on a limited range of data ($0 < 2\theta < 50^\circ$) corresponding to that used for the $R$-factor-map calculations. Both models refined to give good fits, but when the data were extended to $2\theta = 150^\circ$, it was clear that while model $P_{213-(3)}$ fitted very well over the whole profile, $P_{213-(1)}$ fitted poorly.
Table 2. Structural data for Bi₃ReO₈ (e.s.d.'s in parentheses)

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re(1)</td>
<td>4(a)</td>
<td>0.1192(3)</td>
<td>0.1192(3)</td>
</tr>
<tr>
<td>Re(2)</td>
<td>4(a)</td>
<td>0.6192(3)</td>
<td>0.6192(3)</td>
</tr>
<tr>
<td>Bi(1)</td>
<td>12(b)</td>
<td>0.1448(3)</td>
<td>0.3513(3)</td>
</tr>
<tr>
<td>Bi(2)</td>
<td>12(b)</td>
<td>0.1193(3)</td>
<td>0.3513(3)</td>
</tr>
<tr>
<td>O(1)</td>
<td>4(c)</td>
<td>0.0323(6)</td>
<td>0.0323(6)</td>
</tr>
<tr>
<td>O(2)</td>
<td>4(a)</td>
<td>0.5319(6)</td>
<td>0.5319(6)</td>
</tr>
<tr>
<td>O(3)</td>
<td>12(b)</td>
<td>0.1391(5)</td>
<td>0.2543(5)</td>
</tr>
<tr>
<td>O(4)</td>
<td>12(b)</td>
<td>0.6163(6)</td>
<td>0.7589(5)</td>
</tr>
<tr>
<td>O(5)</td>
<td>4(a)</td>
<td>0.2911(5)</td>
<td>0.2911(5)</td>
</tr>
<tr>
<td>O(6)</td>
<td>4(a)</td>
<td>0.7797(5)</td>
<td>0.7797(5)</td>
</tr>
<tr>
<td>O(7)</td>
<td>12(b)</td>
<td>0.2329(5)</td>
<td>0.2140(4)</td>
</tr>
<tr>
<td>O(8)</td>
<td>12(b)</td>
<td>0.2605(6)</td>
<td>0.5999(4)</td>
</tr>
</tbody>
</table>

Above 2θ = 50°. When interatomic distances and angles were calculated, model P2₁3-(1) could be safely rejected since it gave an acceptably low O–O contact of 1.6 Å and metal–O coordinations that were chemically unreasonable. Model P2₁3-(3), however, gave good metal coordination geometries and a closest O–O contact of 2.60 Å. Subsequent calculations on model P2₁3-(3) refining all positional parameters, three thermal parameters (one for each atomic type), and the instrumental parameters gave an R factor (based on intensities, RI = 100 \[\frac{|I_o - I_c|}{I_o}\]) of 5.3% and a profile R factor (\(R_p = 100\frac{\sum|\gamma_o - \gamma_c|}{\sum\gamma_o}\)) of 10.4%. There were no major discrepancies in the calculated profile (Fig. 4).

As a final test, the positions determined from the neutron profile refinement were used in a refinement of the X-ray powder data (which do not suffer from the severe extinction associated with the single-crystal data). After two cycles of refinement of a scale factor and an overall thermal parameter, the R factor (based on intensities) was 5.8%. Because of the severe absorption, the overall thermal parameter refined to a negative value (\(B = -3.0 \text{ Å}^2\)). In subsequent cycles of refinement, the metal-atom positions did not shift by more than one e.s.d., although the O-atom positions, as previously, were unstable.

The structural data are summarized in Table 2, and illustrated in Figs. 5 and 6. Table 3 contains selected interatomic distances and angles.

### Discussion

The structure of Bi₃ReO₈ contains an ordered array of ReO₄ tetrahedra in a distorted fluorite structure. The ReO₄ tetrahedra are slightly deformed, leading to the splitting of the peaks in the infrared spectrum at 900 cm⁻¹, but the bond distances (mean 1.74 Å) are in good agreement with those found in perrhenates. The tetrahedra cluster together, as can be seen from the projection down the (111) direction in Fig. 5. The Bi coordination is open, as found in the com-

![Fig. 4. Calculated (full line), observed (points) and difference profiles from the final refinement of the neutron data. Reflection positions are shown.](image-url)

![Fig. 5. Projection of the structure of Bi₃ReO₈ down (111). For clarity, only the O atoms in the ReO₄ tetrahedra are shown and only one of each pair of atoms related by the approximate body-centring is shown. The projected positions of the remaining O atoms lie near the Bi-atom positions.](image-url)
pounds BiReO$_4$ and BiRe$_2$O$_6$, with three close O atoms (2.1 Å) and one [Bi(1)] or two [Bi(2)] further O atoms at 2.6 Å. The deviations from the ideal cubic coordination are shown in Fig. 7. The major distortion from the ideal fluorite structures comes from the O atoms in the ReO$_4$ tetrahedra (see Table 4).

The cell volume of Bi$_3$ReO$_8$ is about 25% larger than typical fluorite compounds ($a_F = 5.8$ Å compared to $a_F = 5.3$ Å for α-Er$_3$ReO$_8$). The metal–O distances in an undistorted fluorite structure of this size would be 2.5 Å. Since the ReO$_4$ tetrahedra, which account for 50% of the O atoms, have Re–O distances of 1.74 Å, one might have expected a slightly smaller volume. It is also difficult for the same reason to explain the rotation of the ReO$_4$ tetrahedra by 40° about [111] (see above). We were able to account for anomalies in volume in Bi$_3$ReO$_8$ and BiRe$_2$O$_6$ in terms of a stereochemically active Bi lone pair (Rae Smith & Cheetham, 1979), and vacant anion sites could be identified in both these structures to accommodate it. When the occupied volume in Bi$_3$ReO$_8$ is examined, there is a site about 1 Å from each Bi atom [for Bi(1) the approximate position is (0.314, 0.324, 0.102)] which could accommodate the lone pair. These sites are related to ideal fluorite anion sites [(1, 1, 0), etc.] by displacements of 1-6 Å towards the Bi atoms, and fall between the O atoms at the base of the ReO$_4$ tetrahedra.

The structures of the closest analogues to Bi$_3$ReO$_8$, the rare-earth rhenium oxides Ln$_3$ReO$_8$, have all been determined and fall into two main types. The low-pressure α-form of Ln$_3$ReO$_8$ (Ln = Tb–Lu, Y) appears to be a disordered fluorite phase (Baud & Besse, 1974) and has a very small range of thermal stability (323 K), while the early rare-earth compounds [Ln = La (Baud, Besse, Chevalier & Gasperin, 1979; Rae Smith, Cheetham & Fuess, 1984), Ce–Gd (Besse, Bolte, Baud & Chevalier, 1976)] and the high-pressure β-form of the later rare-earth compounds [Ln = Tb–Lu, Y (Baud, Besse, Chevalier & Gasperin, 1981)] have closely related structures which can be described in terms of an ordered fluorite substructure. The early rare-earth compounds resemble Bi$_3$ReO$_8$ in their high thermal stability, but their structures are essentially different from Bi$_3$ReO$_8$ in that they contain octahedrally coordinated Re. Bi$_3$ReO$_8$ thus appears to have a unique structure.

We wish to thank Hermann Starck Berlin for the provision of rhenium, and the SERC for the provision of neutron and computing facilities.

One of us (ARRS) is pleased to acknowledge support through National Science Foundation Grant DMR 8108306 for the completion of this work.

Table 4. Deviations from ideal fluorite positions (Å)

<table>
<thead>
<tr>
<th></th>
<th>Re(1)</th>
<th>0.12</th>
<th>Re(2)</th>
<th>0.12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(1)</td>
<td>0.39</td>
<td></td>
<td>Bi(2)</td>
<td>0.34</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.65</td>
<td></td>
<td>O(2)</td>
<td>0.64</td>
</tr>
<tr>
<td>O(3)</td>
<td>1.45</td>
<td></td>
<td>O(4)</td>
<td>1.56</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.83</td>
<td></td>
<td>O(6)</td>
<td>0.60</td>
</tr>
<tr>
<td>O(7)</td>
<td>0.47</td>
<td></td>
<td>O(8)</td>
<td>0.48</td>
</tr>
</tbody>
</table>

The structures of the closest analogues to Bi$_3$ReO$_8$, the rare-earth rhenium oxides Ln$_3$ReO$_8$, have all been determined and fall into two main types. The low-pressure α-form of Ln$_3$ReO$_8$ (Ln = Tb–Lu, Y) appears to be a disordered fluorite phase (Baud & Besse, 1974) and has a very small range of thermal stability (323 K), while the early rare-earth compounds [Ln = La (Baud, Besse, Chevalier & Gasperin, 1979; Rae Smith, Cheetham & Fuess, 1984), Ce–Gd (Besse, Bolte, Baud & Chevalier, 1976)] and the high-pressure β-form of the later rare-earth compounds [Ln = Tb–Lu, Y (Baud, Besse, Chevalier & Gasperin, 1981)] have closely related structures which can be described in terms of an ordered fluorite substructure. The early rare-earth compounds resemble Bi$_3$ReO$_8$ in their high thermal stability, but their structures are essentially different from Bi$_3$ReO$_8$ in that they contain octahedrally coordinated Re. Bi$_3$ReO$_8$ thus appears to have a unique structure.

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References