Structure of BiRe$_2$O$_6$ re-investigated using single-crystal neutron Laue diffraction

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Abstract. Single crystals of BiRe$_2$O$_6$ of typical volume 0.03 mm$^3$ were grown by chemical vapor transport and characterized using room-temperature single-crystal neutron diffraction in monoclinic $C2/c$ symmetry with cell parameters $a = 16.1178(11)$ Å, $b = 4.9235(3)$ Å, $c = 5.5278(3)$ Å and $\beta = 92.475(5)$ ° ($R_{all} = 11.39$ and $wR_{all} = 7.97$). The structure contains ordered layers of corner sharing units of Re$_2$O$_{10}$ with Re-Re distances of 2.519(1) Å. The unit cell is doubled along $c$ in comparison to previous studies based on X-ray diffraction data where the layer stacking was described as disordered.

1. Introduction

Rhenium has been reported in oxidation states of 4$^+$ [1], 4$^+$/5$^+$ [2-4], 5$^+$ [2,3], 5$^+$/6$^+$ [5] and 7$^+$ [6,7] in ternary compounds. Re$^{5+}$-containing compounds are generally synthesized in atmospheric conditions and feature 5$d^0$ electronic configuration of Re. The other oxidation states of Re, which contain 5$d$ electrons, are synthesized under a variety of reducing conditions. The high-spin versions of these compounds are of interest for their magnetic properties, and in particular for what has been termed “unconventional rhenium magnetism.” [8]

BiRe$^{5+}$O$_4$ [2,3], BiRe$^{4+}$/5$^+$O$_{11}$ [2] and Bi$_3$Re$^{4+}$/5$^+$O$_{11}$ [2] are known examples with unpaired $d$ electrons on Re. BiRe$_2$O$_6$ [2,3] has a KSB$_2$O$_3$-related structure previously observed in SbRe$_2$O$_6$, [9] ScRe$_2$O$_6$ [8] and Sb(Nb/Ta)TiO$_6$. [10] These compounds all feature edge-sharing Re$_2$O$_{10}$ octahedral dimers that form layers by sharing corners with other dimers. [5] The Re–Re bond within the dimers often results in metallic behavior and good electrical conductivity. [8] The Re–Re bond lengths vary from 2.415(1) Å in La$_4$Re$_2$O$_{19}$[4] to 3.102(1) Å in PbRe$_2$O$_6$. [11]

Initial work on BiRe$_2$O$_6$ by Cheetham and Smith [3] proposed a monoclinic $C2/m$ cell with $a = 5.516(1)$, $b = 4.906(1)$, $c = 8.384(1)$ Å and $\beta = 106.71(1)$ °. A disordered stacking of the Re–O layers was described. Some Weissenberg photographs contained weak reflections suggesting a doubling of the $c$ axis, but they did not contain enough significant intensity to be used in refinements. Bi is found
in distorted square pyramidal and distorted octahedral environments depending on the relative orientation of the Re–O layers.

Here, we have re-investigated the structure of BiRe$_2$O$_6$ by single-crystal neutron diffraction, after synthesizing sufficiently large crystals for the white-beam Laue technique used by the instruments VIVALDI at the Institut Laue-Langevin (ILL) Grenoble, France [12], and KOALA at the Open-Pool Australian Light-water reactor (OPAL), Lucas Heights, Australia.

2. Experimental

Chemical vapor transport was used to synthesize crystals of BiRe$_2$O$_6$. Bi$_9$ReO$_{17}$ [7] and Re metal were pre-reacted in evacuated sealed quartz tubes for 4 days at 800 °C. This mixture was combined with the NH$_4$Br transport agent and placed at the source position of a quartz tube. The quartz tube was then evacuated and sealed. The source position of the tube was heated to 650 - 750 °C, while the sink position was maintained 50 °C lower in temperature. The reaction proceeded for 5 days.

Crystals were initially analyzed on a Bruker-Nonius APEX II X-ray diffractometer with Mo $K_a$ radiation ($\lambda = 0.71073$ Å). Preliminary neutron Laue data were collected at room temperature on VIVALDI at the ILL, followed by the collection of a more complete data set on KOALA at OPAL. VIVALDI and KOALA use ‘white’ thermal-neutron beams (0.8 Å $\leq \lambda \leq$ 5.2 Å) with cylindrical image-plate detectors. The same 0.3×1.0×0.1 mm crystal mounted on a vanadium pin was used for data collection on both instruments.

Neutron Laue patterns were collected on KOALA in 12 exposures of 2 h each, separated by 12° rotations of the $\phi$-axis (perpendicular to the neutron beam), providing good data redundancy and completeness. The patterns were indexed using the program LAUEGEN [13], and the reflections integrated using ARGONNE_BOXES [14] and normalised to a common wavelength using LAUENORM. [15] The reduced data contained 4322 reflections (2084 unique) in the ranges $-29 \leq h \leq 29$, $0 \leq k \leq 8$, $0 \leq l \leq 8$. Structural refinements were undertaken with the Jana2006 [16] package.

3. Results and Discussion

The fact that these crystals can only be obtained in small quantities by chemical vapor transport presents an unusual situation for structural analysis, where single-crystal neutron diffraction using VIVALDI and KOALA was feasible, but insufficient total quantities were available for neutron powder diffraction (after grinding up the crystals). The majority of the crystals tested on VIVALDI were laminated perpendicular to the stacking axis $a$, but a suitable candidate for full data collection was identified from the 10 tested.

The single-crystal neutron Laue patterns clearly showed reflections corresponding to a doubling of the $c$ axis of the reported [3] unit cell. The standard setting for this enlarged cell (in which $a$ and $c$ are exchanged with respect to that of Cheetham et al. [3]) is monoclinic $C2/c$ $a = 16.1178(11)$, $b = 4.9235(3)$, $c = 5.5278(3)$ Å and $\beta = 92.475(5)$ °. Using SbRe$_2$O$_6$ [9] as a starting model, the positions and independent anisotropic atomic displacement parameters (ADP’s) could be refined for all atoms. Final statistics for 43 refined parameters were $R_{\text{all}} = 11.39 \%$, $R_{\text{obs}} = 7.08 \%$, $wR_{\text{all}} = 9.97 \%$, and $wR_{\text{obs}} = 7.82 \%$. Refined atomic parameters, ADP’s, and bond valence sums (BVS) [17] are presented in table 1 and bond lengths and angles are presented in table 2. Figure 1 shows the refined structural model of BiRe$_2$O$_6$.

Table 1. Final refined fractional atomic coordinates, ADP’s, and bond valence sums (BVS) for BiRe$_2$O$_6$ in $C2/c$, $a = 16.1178(11)$, $b = 4.9235(3)$, $c = 5.5278(3)$ Å and $\beta = 92.475(5)$ ° with $Z = 4$.

| Atom | Wyckoff position | $x$   | $y$   | $z$  | $100 \times U_{eq}/U_{iso}$ | BVS |
|------|------------------|-------|-------|------|----------------------------|------|
| Bi   | 4$a$             | 0.0   | 0.2735(2) | 0.25 | 0.75(4) | 3.35(1) |
| Re   | 8$b$             | 0.1804(1) | 0.2356(2) | -0.1129(2) | 0.22(2) | 4.53(1) |
| O1   | 8$b$             | 0.2156(1) | 0.4769(2) | 0.1690(3) | 0.62(4) | 2.13(1) |
| O2   | 8$b$             | 0.1378(1) | -0.0300(3) | 0.1087(3) | 0.75(4) | 1.80(1) |
| O3   | 8$b$             | 0.0699(1) | 0.4044(3) | -0.0836(3) | 0.81(4) | 2.27(1) |
Table 2. Selected metal–oxygen bond lengths (Å) in the refined structure of BiRe₂O₆.

| Bond     | Length (Å) |
|----------|------------|
| Bi - O1  | 2.799(1) × 2 |
| Bi - O3  | 2.270(1) × 2 |
| Bi - O3  | 2.129(2) × 2 |
| Re - Re  | 2.519(1)   |
| Re - O1  | 2.014(1)   |
| Re - O1  | 1.999(2)   |
| Re - O1  | 1.947(2)   |
| Re - O2  | 1.935(2)   |
| Re - O2  | 1.926(2)   |
| Re - O3  | 1.970(1)   |

Figure 1. The crystal structure of BiRe₂O₆ with Bi in light gray, edge-sharing octahedral Re₂O₁₀ groups in dark gray and Re illustrated as gray spheres. The structure viewed along the (a) [010] and (b) [011] direction.

Our model shows the presence of ordered stacking of layers of Re₂O₁₀ dimers to form two-dimensional layers. The Re–Re bonds in this structure are 2.519(1) Å, a value which is intermediate between those found in SbRe₂O₆ and ScRe₂O₆. [8,9] Re–O bonds range from 1.926(2) to 2.014(1) Å. The BVS’s indicate chemically plausible coordination environments for all ions, including Re⁴⁺, and the Bi–O distances and coordination environments (figure 2) are all reasonable.
Figure 2. The coordination environments of Bi and Re viewed along the [001] direction in the refined structure of BiRe$_2$O$_6$. Re-Re bond is also shown.

4. Conclusions

Single-crystal neutron Laue diffraction is a powerful technique for solving and refining the structures of compounds that require neutron (rather than X-ray) diffraction data, but for which it is not possible to obtain sufficient quantities for neutron powder diffraction. Such a situation arose in this case due to the use of chemical vapor transport synthesis. Data collected on VIVALDI and KOALA were used to identify and refine the ordered superstructure of BiRe$_2$O$_6$, in which Re$_2$O$_{10}$ edge-sharing octahedral dimers are ordered into two-dimensional layers separated by Bi atoms with square pyramidal coordination.

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