Structural Variations of BiMnO$_{3+x}$ Revealed by Electron Diffraction

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Abstract. Electron diffraction studies have been performed on a number of samples within the series BiMnO$_{3+x}$ (for the range $-0.11 < x < 0.16$). Samples with a large value of $x$ (either positive or negative) crystallize as a monoclinic perovskite supercell structure not dissimilar from the stoichiometric ideal. However, the variation of oxygen composition manifests itself as disorder in either the cation or anion sub-lattices, leading to a reduction in symmetry (to $C_2$, $P_2_1$ or $P_2$). In addition, three new structures have been identified at compositions closer to the perovskite ideal. One structure is similar to a mixed cation phase reported by Hughes et al., while another is an $n=2$ Ruddlesden-Popper phase; importantly both of these phases are acentric and so could support multiferroic properties. The third is as yet not fully characterised but seems to crystallise into a different monoclinic structure than the stoichiometric ideal phase.

1. Introduction

Bismuth manganite is a perovskite-based material that has been proposed as a possible alternative to bismuth ferrite for multiferroic applications [1, 2]. While the ferromagnetic properties of iron and manganese oxides are well known it is the presence of bismuth that makes these materials candidates also for ferroelectricity. A lone pair of electrons allows the Bi$^{3+}$ ion to reside away from the centre of the perovskite unit, thus allowing possible ferroelectric polarisation. While this is true for bismuth ferrite, studies on stoichiometric bismuth manganite seem to suggest that the structure forms a stable monoclinic structure with cell parameters $a = 9.532\,\text{Å}$, $b = 5.606\,\text{Å}$, $c = 9.854\,\text{Å}$, $\beta = 110.67^\circ$, and space-group $C2/c$. This space-group is centrosymmetric and so cannot support ferroelectricity, however there have been conflicting reports of bismuth manganite samples exhibiting ferroelectric polarisation [3].

One possible explanation from Belik et al. [4] is that the structure has a space-group of $C2/c$ but that there are local domains within this structure where the symmetry is lowered to $C2$ or $P2_1$, shown by previously forbidden reflections existing at high temperatures and after the incorporation of additional elements into the structure. These mechanisms suggest that by incorporating vacancies into the manganese or oxygen sub-lattices of the structure, it is possible to reduce the overall symmetry of the structure, potentially allowing a non-centrosymmetric structure to be stable for the material.

2. Experimental Details

Electron diffraction studies were performed on a number of bismuth managanite BiMnO$_{3+x}$ samples with oxygen deviation ($x$) varying from -0.11 to 0.16. The majority of experiments,
Figure 1. SAED patterns recorded parallel to the [010] axis of bismuth manganite samples. a) BiMnO$_3$.00. HOLZ reflections are shown as inset and identify the $c$-glide present. b) BiMnO$_2$.89. The indicated reflections show the $h0l, l = 2n$ condition for allowed reflections. c) BiMnO$_3$.16. Weak reflections show that there are no forbidden reflection conditions in this projection.

including all precession electron diffraction (PED), were undertaken on a Philips CM30 TEM with a Nanomegas Spinningstar Precession device. Some additional work performed on a Philips CM300 FEGTEM. There have been reports of bismuth manganite undergoing structural transformations under high energy electron irradiation [5] so all TEM operation was performed at 150kV. All diffraction patterns were recorded on Ditabis Imaging Plates

3. Results and Discussion

3.1. Monoclinic Bismuth Manganite Samples

3.1.1. BiMnO$_3$.00. As a comparison with the expected structure, a sample of stoichiometrically ideal BiMnO$_3$ was examined. Figure 1a shows a SAED pattern recorded parallel to the monoclinic [010] axis of the structure. The basis vectors are indicated and from this pattern it is possible to determine the cell parameters of the material to be $a = 8.63\,\text{Å}$, $b = 5.85\,\text{Å}$, $c = 8.97\,\text{Å}$, $\beta = 110.1^\circ$, showing good agreement with the accepted values. The reflection condition for the ZOLZ layer is $h0l, h, l = 2n$. Given the offset of the HOLZ reflections, the allowed reflections in the $l$-direction in the HOLZ and a diad rotation axis (indicated by the whole pattern symmetry) the only allowed space-group is $C2/c$.

3.1.2. BiMnO$_2$.89. To determine the symmetry of the sample with composition BiMnO$_2$.89 the [010] zone axis was investigated. The SAED pattern for this is shown in Figure 1b, unlike the stoichiometric ideal phase, this bismuth manganite structure has been distorted (by vacancy ordering on the oxygen sub-lattice) and the reflection condition for $h0l$ has changed to $l = 2n$ only. Without a full structural analysis it is not possible to identify the space-group although it is restricted to $C2$ or $P2_1$, and so is likely to be non-centrosymmetric despite the similarity to the parent structure. As with the reported study [4], the weakness of these reflections suggest that these additional reflections are not present throughout the sample but might be caused by some sort of local domain structure.

3.1.3. BiMnO$_3$.16. As with the previous samples the zone axis pattern parallel to [010] was used to identify the major features of the space-group symmetry of the sample. In the case where the oxygen stoichiometry is greater than the ideal value of 3.0 the diffraction pattern (shown in Figure 1c) shows a further reduction in the overall symmetry, in this case there are no reflections forbidden in the [010] zone axis diffraction pattern allowing only $P2$ or $P2_1$ as possible
Figure 2. CBED patterns from the BiMnO$_{2.99}$ sample recorded parallel to a) [010], b) [100] and c) approximately 21° along [010] from [100].

space-groups, suggesting a possible acentric structure. The ‘extra’ reflections (compared to the stoichiometric ideal pattern Figure 1a) in this pattern are much more strongly defined which suggests that any ordering of vacancies on the manganese sub-lattice is not confined to small domains, as the BiMnO$_{2.89}$ sample, but is a more general feature of the samples structure.

3.2. Orthorhombic and Other Structure Variants of Bismuth Manganite

3.2.1. BiMnO$_{2.99}$ Despite its compositional similarity to the ideal bismuth manganite structure, a slightly deoxygenated sample, BiMnO$_{2.99}$, crystallized into a large orthorhombic cell with approximate cell parameters, $a = 15.6$Å, $b = 5.52$Å, $c = 11.1$Å, (determined from CBED patterns shown in Figures 2a and b). These cell parameters suggest that the structure is similar to a mixed cation perovskite Bi(Mn/Ni)O$_3$ [6]. There are compositional similarities that could explain why this structure is common to both systems: the removal of oxygen from the perovskite structure will lead to a reduction in the total oxidation state of the manganese, which is comparable to the incorporation of a divalent ion such as nickel in the place of a trivalent manganese ion. While the reported structure has equal amounts of manganese and nickel on the sublattice it seems that a small oxygen deficiency is also capable of stabilising this structure [7].

Figure 2c shows a CBED pattern recorded after tilting by approximately 21° along [010] from the [100] zone axis of the BiMnO$_{2.99}$ sample. The long extinction lengths of HOLZ reflections make them more sensitive to subtle symmetry breaking and this, combined with the reflection conditions from Figures 2a and b, allows the space-group of the structure to be identified as $P_{nm}$, a non-centrosymmetric space-group. While this structure does seem to be quite different to the monoclinic perovskite superlattice seen for the first three samples, it is interesting to note that the [010] zone-axis diffraction pattern from this sample is similar to the [010] zone axis pattern from the BiMnO$_{3.16}$ sample. A small change in the symmetry of ions occupying the manganese sublattice can account for this change and so there seems to be a strong structural link between these two phases.

3.2.2. BiMnO$_{3.10}$ The superoxygenated sample (BiMnO$_{3.10}$) is a mixed phase sample. One component phase is a non-centrosymmetric $n$=2 Ruddlesden-Popper structure (seen in other mixed phase bismuth manganite samples [7]) identified from Figures 3a, a PED pattern recorded parallel to the [001] zone-axis of this structure. The structure of the secondary phase in this structure has not yet been fully determined, the evidence in Figure 3b suggests that this is a monoclinic supercell with cell parameters $a = 9.60$Å, $b = 5.32$Å, $c = 9.81$Å, $\beta = 109.7^\circ$. The CBED pattern in Figure 3c has clear Gjonnes-Moodie lines indicating $P2_{1}/c$ as the space-group. To remain consistent
Figure 3. Electron diffraction patterns from the BiMnO$_{3.10}$ sample. a) is a PED pattern from an n=2 Ruddlesden-Popper phase recorded parallel to [001], b) PED and c) CBED are from a new monoclinic phase; patterns were recorded parallel to [010] and [100] respectively.

with the [100] zone-axis pattern the reflection conditions in the [010] zone axis pattern have to be $h0l$, $l = 2n$.

4. Conclusions
For multiferroic properties to exist in a sample it is vital that a non-centrosymmetric crystal structure can be supported. While it is clear that stoichiometric bismuth manganite cannot (under ambient conditions) support ferroelectricity because of the centrosymmetric space-group, it is clear that small variations in composition can lead to significant changes in the structure of the material. It is clear that full understanding of the structural transitions between the linked $C2/c$, $P2$ (or $P2_1$) and $Pnm21$ phases is important and could enable the oxygen composition to be tuned to create phases with a non-centrosymmetric structure, and possible multiferroic behaviour. The Ruddlesden-Popper phase seen in this series is also of great interest as it is non-centrosymmetric and to date seen only in two-phase samples. Understanding how the two phases arise from a single precursor will be important to enable specific structures to be synthesized from within the bismuth manganite system. Further work is needed to refine the structures of the monoclinic phases present in the BiMnO$_{2.89}$ and BiMnO$_{3.10}$ samples.

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