A careful phase analysis and TEM investigation of the incommensurately modulated, \((Bi_{1-x}M)^{III}Fe^{III}O_{3-x/2} (M = Ca and Sr)\), solid solution phases

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Abstract. A careful phase analysis and TEM investigation of the \((Bi_{1-x}Ca)^{III}Fe^{III}O_{3-x/2}V_{x/2} (V\ for\ vacancy)\), \(-0.20 \leq x \leq -0.50\), and \((Bi_{1-x}Sr)^{III}Fe^{III}O_{3-x/2}V_{x/2}\), \(0.2 \leq x \leq 0.67\), perovskite related solid solution fields has been carried out. Both solid solution fields are, in general, \((3+1)-d\) incommensurately modulated with an incommensurate primary modulation wave-vector magnitude that varies systematically with composition. High Resolution (HR)TEM imaging is used to show the presence of at least 6-fold twinning on a sometimes rather fine scale, the fine scale twinning being more prevalent in the \(M = Sr\) than the \(M = Ca\) system. The \((3+1)-d\) superspace group symmetry is suggested to be \(Cmmm\ (01\gamma)\ 0s0\) or one of the non-centrosymmetric sub-groups thereof. The magnetic and electrical properties of the systems are briefly discussed and a tentative structural model proposed.

1. Introduction

Bismuth ferrite \((BiFeO_3)\) exhibits multiferroic properties at room temperature and is a promising lead-free piezoelectric material. A major drawback with BiFeO\(_3\), however, is its high current leakage. Attempts to improve its electrical properties have been made by substitutional doping with a range of rare earth as well as alkaline earth elements on the Bi, or perovskite A, site. In this paper, the results of a careful phase analysis, Transmission Electron Microscope (TEM) and physical properties investigation of the alkaline earth substituted, wide range non-stoichiometric \((Bi_{1-x}Ca)^{III}Fe^{III}O_{3-x/2}V_{x/2}\) (\(V\ for\ vacancy\), \(-0.2 \leq x \leq -0.5\), and isomorphous \((Bi_{1-x}Sr)^{III}Fe^{III}O_{3-x/2}V_{x/2}\), \(0.2 \leq x \leq 0.67\), perovskite related solid solution phases are reported.

2. Synthesis and phase analysis

The \(M = Sr\) sample was prepared by conventional solid state reaction (see Withers \textit{et al} [1]). The \(M = Ca\) samples were prepared by a rapid two-stage reaction method using high purity Bi\(_2\)O\(_3\), CaCO\(_3\) and Fe\(_2\)O\(_3\) powders, following Khomchenko \textit{et al} [2]. The starting powders were initially homogenized for \(-20\) minutes in an agate mortar before a first reaction at \(-850\ ^\circ\)C for \(-20\) minutes. The resultant samples were then re-ground for a further \(-20\) min, pressed into pellets at \(-480\ MPa\) in a steel die and sintered for a further \(-20\) minutes according to composition. Samples with \(-0.3\) were sintered at \(-940\ ^\circ\)C while
samples with $x > 0.3$ were sintered at 990 °C. Use of sintering temperatures above these caused melting of the samples. Despite the surprisingly short reaction times, extremely well-crystallized reaction products were obtained via this process.

The signature of a continuously variable solid solution phase, namely composition-dependent, continuously variable, unit cell dimensions, is observed in both systems. The metric symmetry of the well-defined, perovskite-related parent (subscript $p$ below), or average, structure of the $M = \text{Ca}$ phase was tetragonal (with the $c_p$ dimension always slightly larger than the $a_p = b_p$ dimension, see Fig.1) but very close to metrically cubic while the metric symmetry of the underlying average structure of the $M = \text{Sr}$ sample was cubic (see also [3]). No additional satellite reflections were apparent in powder XRD patterns from either solid solution phase. Fig.1 shows a plot of the powder XRD refined metrically tetragonal unit cell dimensions of the underlying perovskite-related, parent structure of the $M = \text{Ca}$ phase as a function of the Ca content, $x$. Note that the lines drawn through the data points in Fig.1 are a guide to the eye only. Samples synthesized outside the shaded composition range were clearly two phase and enabled the composition range of existence of the $M = \text{Ca}$ phase to be determined to run from $\sim 0.20 \leq x \leq \sim 0.50$. In the case of the $M = \text{Sr}$ phase, the corresponding composition range of existence is somewhat broader, namely from $\sim 0.20 \leq x \leq \sim 0.67$ [3].

![Fig.1](image)

**Fig.1** Shows the XRD refined, metrically tetragonal unit cell dimensions, $a_p = b_p$ (solid squares) and $c_p$ (open circles), of the parent structure of the $M = \text{Ca}$ phase as a function of Ca content, $x$.

### 3. HRTEM imaging and twinning

Despite the metric symmetries, both solid solution phases are, in general, $(3+1)$-d incommensurately modulated with a primitive primary modulation wave-vector $q_{\text{prim}} = \frac{1}{2}b_p^* + \gamma c_p^*$ that varies systematically with composition [4]. The local symmetry is thus at most orthorhombic. The higher apparent symmetry of the underlying average structures arises from inherent fine scale twinning, particularly in the case of the $M = \text{Sr}$ phase. Fig.2a, for example, shows a typical $<100>_p$ zone axis HRTEM image of an $x = 0.46$, $M = \text{Sr}$ sample along with the corresponding Fast Fourier Transform (FFT) of the whole image. Incommensurate 'superlattice fringes' of periodicity $a_p/(1 - 2\gamma) \sim 3.47a_p \sim 13.7 \text{ Å}$, running largely along only one or other of the two $<001>_p$ directions of reciprocal space excited in any one such $<100>_p$ type image (and corresponding to the incommensurate satellite reflections apparent in the FFT, see Fig.2b), are clearly apparent. In other areas, no obvious superlattice fringes are apparent at all suggesting that the incommensurate component of the modulation in such regions is running along the third $<001>_p$ direction of reciprocal space *i.e.* along the projection direction. Thus the $M = \text{Sr}$ phase is at least triply twinned
on quite a fine, ~5-10 nm, scale. It is thus clear that the incommensurate component of the primitive primary modulation wave-vector runs along only one of the three possible \( <001>_p \) directions in any one local region.

Fig.2. Shows a typical (a) \(<100> \) zone axis HRTEM image of an \( x = 0.46, \gamma = 0.356(1), M = \text{Sr} \) sample along with (b) the corresponding Fast Fourier Transform (FFT) of the whole image.

In addition to this form of twinning, a rather more subtle form of twinning occurs in both phases involving a switch in the primitive primary modulation wave-vector from \([0, 1/2, \gamma]_p^* \) to \([1/2, 0, \gamma]_p^* \). Such twinning is apparent in the change in periodicity along the superlattice fringes themselves from \( b_p \) to \( 2b_p \) as can be seen in going from the bottom left to the top right hand side of the \(<100>_p \) zone axis HRTEM image of an \( x = 0.36, \gamma = 0.4, M = \text{Ca} \) grain shown in Fig.3 below.

Fig.3. A \(<100>_p \) zone axis HRTEM image of an \( x = 0.36, \gamma = 0.4, M = \text{Ca} \) grain. Note the change in periodicity along the superlattice fringes from the bottom left to the top right hand side of the image.

4. Electron diffraction and superspace group symmetry.

Given the prevalence of twinning even in the \( M = \text{Ca} \) case, it is not surprising that selected area electron diffraction patterns (EDP's) are almost invariably twinned (see, for example, the typical
<001>, p type zone axis EDP's shown in Figs. 4a to c below) making it rather difficult to unambiguously determine the corresponding (3+1)-d superspace group symmetry.

![Fig. 4](image)

Fig. 4. Shows typical <001>, p type zone axis EDP's with values of (a) 0.386(1), (b) 0.375(1) and (c) 0.417(1) found in x = 0.333, 0.375 and 0.25, M = Ca samples. (d) shows a typical <-110>, p zone axis EDP of an x = 0.2 sample with γ = 0.417(1). Indexation in all cases is with respect to the (3+1)-d reciprocal lattice basis vector set M* = \{\frac{1}{2}a_p^*, \frac{1}{2}b_p^*, \frac{1}{2}c_p^*, q = γc_p^*\}.

In addition to the strong Bragg reflections of the underlying perovskite-related parent structure, labelled G hereafter, there are a host of additional (in general, incommensurate) satellite reflections characterized by the composition-dependent, primitive primary modulation wave-vector q_{prim} = \frac{1}{2}b_p^* + γc_p^* (see e.g. the reflections labelled 0101, 0202 etc. in Fig. 4a). These satellite reflections arise from coupled O/V (V an oxygen vacancy) and Bi/Ca ordering and associated structural relaxation [1,5]. In addition to these G ± m q_{prim} (m an integer) satellite reflections, G ± \frac{1}{2} <110>_p^* (arrowed but not labelled in Fig. 4a) as well as G ± \frac{1}{2} [111]_p^* (see e.g. the reflection labelled 1110 in Fig. 4d) Bragg reflections are also, in general, present. The same is also true for the M = Sr solid solution. Indexation in Fig. 4 is thus with respect to the (3+1)-d reciprocal lattice basis set M* = \{\frac{1}{2}a_p^*, \frac{1}{2}b_p^*, \frac{1}{2}c_p^*, q = γc_p^*\}. The presence of the G ± \frac{1}{2} [111]_p^* reflections is presumably either a weak structural response to the G-type anti-ferromagnetic ordering of the Fe moments associated with the wave-vector \frac{1}{2} [111]_p^* (see e.g. [6]) or are associated with polyhedral rotations. The
$G \pm \frac{1}{2} <110>_p^*$ reflections are presumably associated with polyhedral rotations and associated structural relaxation. Weak incommensurate satellite reflections of even order are observed around the $G \pm \frac{1}{2} <110>_p^*$ reflections (see e.g. the reflection labelled 1102 in Fig.4d) but no satellite reflections at all are observed around the $G \pm \frac{1}{2} [111]_p^*$ reflections (see also Fig.4d).

The absence of the $G \pm \frac{1}{2} <110>_p^*$ Bragg reflections in the twinned $<100>_p$ type zone axis EDP shown in Fig.4c suggests that these reflections are of $G \pm \frac{1}{2} [110]_p^*$ type and only exist in the Zero Order Laue Zone at the $[001]_p$ zone axis orientation. This is also consistent with the apparently single domain $[001]_p$ zone axis FFT of an $x = 0.667, M = \text{Sr}$ sample reported in Fig.3b of [5]. The systematic extinction conditions characteristic of both solid solution phases are then $F(HKLM) = 0$ unless $H+K+M$ is even and $F(H0LM) = 0$ unless $H, M$ both even implying the superspace group symmetry $Cmmm(01\gamma)0s0$ (a non-standard setting of $Cmmn(10\gamma)s00$, see [7]) or one of the non-centrosymmetric sub-groups thereof. Note that ferroelectric ordering would require one of the latter sub-group symmetries and rule out the former. The $Pmmm(01/2\gamma)0s0$ superspace symmetry previously suggested for the $M = \text{Sr}$ solid solution [1] excluded the presence of the weak $G \pm \frac{1}{2} [110]_p^*$ and $G \pm \frac{1}{2} [111]_p^*$ reflections. When these reflections are included the superspace group symmetry $Cmmm(01\gamma)0s0$ as described above is obtained i.e. the $M = \text{Ca}$ and Sr solid solutions are isomorphous. Finally, note that the anti-ferromagnetic ordering associated with the modulation wave-vector $\frac{1}{2} [111]_p^*$ (see e.g. [6]) is not described by the above superspace group symmetries.

5. Properties measurements

The measured room temperature magnetizations of $M = \text{Ca}, x = 0.20, 0.36$ and 0.50, samples (in Bohr magnetons/formula unit) as a function of applied field are shown in Fig.5.

![Figure 5](image_url)

Fig.5. The measured room temperature magnetization of $M = \text{Ca}, x = 0.20, 0.36$ and 0.50, samples (in Bohr magnetons/formula unit) as a function of applied field.

The consistent measured magnetization for these samples up to 7 kG indicates that there is no change in iron valence state throughout the solid solution range, as also supported by Mössbauer measurements. Ferroelectric hysteresis loops of the $M = \text{Ca}$ samples could not be obtained at room temperature and zero magnetic field as a result of the intrinsic semiconductivity of the materials. This does not, however, necessarily preclude the existence of co-ordinated ferroic type ion displacements. Kundys et al [7], for example, have reported magnetic field induced ferroelectric behavior for the $M =$
Sr phase. Likewise, bond valence sum calculations on the structural model proposed below suggest a need for off-centre Bi ion displacements in the central BiFeO$_3$-like part of the structure.

6. A suggested structural model

A previously suggested structural model for the solid solution phase [1] involving octahedral as well as square pyramidal Fe co-ordination was found not to fit to the observed HRTEM images of the $M = \text{Ca}$ samples or to the three distinct Fe co-ordination environments required by Mossbauer results [4]. An alternative disordered variant of the two symmetry-equivalent model structures shown in Fig.6 below, however, does fit quite well with the observed HRTEM images as well as being consistent with the overall stoichiometry and the Mossbauer results [4].

Fig.6. Shows [100] projections of various models for $\gamma = 2/5$, corresponding to a 5 x superlattice along c$_p$ (vertical) and to HRTEM images such as that shown in Fig.3. The oxygen vacancies are represented by the open squares, the Bi ions by the large balls, the Ca ions by the medium sized balls and the oxygen ions by the smallest sized balls, green for half occupied and red for fully occupied.

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