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Chap. 7 : Naturally Layered Aurivillius Phases: Flexible Scaffolds for the Design of Multiferroic Materials

J. Halpin (1) and L. Keeney (1)

(1) Tyndall National Institute, University College Cork, Ireland

Corresponding author : lynette.keeney@tyndall.ie

Abstract : The Aurivillius layer-structures, described by the general formula $\text{Bi}_2\text{O}_2(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$, are naturally 2-dimensionally nanostructured. They are very flexible frameworks for a wide variety of applications, given that different types of cations can be accommodated both at the A- and B-sites. In this review article, we describe how the Aurivillius phases are a particularly attractive class of oxides for the design of prospective single phase multiferroic systems for multi-state data storage applications, as they offer the potential to include substantial amounts of magnetic cations within a strongly ferroelectric system. The ability to vary m yields differing numbers of symmetrically distinct B-site locations over which the magnetic cations can be distributed and generates driving forces for cation partitioning and magnetic ordering. We discuss how out-of-phase boundary and stacking fault defects can further influence local stoichiometry and the extent of cation partitioning in these intriguing material systems.

Keywords : AURIVILLIUS, FERROELECTRIC, MULTIFERROIC, MAGNETIC CATION PARTITIONING

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I. Introduction

The aim of this review is to introduce the Aurivillius phase materials, highlight current areas of research and to provide a concise overview of the versatility of the Aurivillius structure. The Aurivillius family of bismuth layered oxides consists of a number of perovskite blocks (ABO_3) separated by a Bi_2O_2 interlayer. The atoms at the *A* and *B* sites of the perovskites can vary within certain size and valence ranges. These materials have a preference for growth in the *c*-axis direction creating a 2-dimensional structure (see Fig. 2) and possess anisotropic properties. This review will highlight the parameters, both chemical and physical, which can be adjusted to tailor the properties of these versatile materials. Commonly studied Aurivillius structures include $Bi_4Ti_3O_{12}$, $SrBi_4Ti_4O_{15}$ and Bi_2WO_6 . There is significant potential for these materials in technological applications. The flexibility of the chemical and structural properties of Aurivillius structures provides the opportunity to tailor these materials towards targeted applications including piezoelectric sensing devices, non-volatile data storage and photocatalytic activities. The Aurivillius phase materials were first identified by Bengt Aurivillius in 1949 (1). These materials have been studied for almost 70 years and over the last two decades have received increasing attention as lead-free ferroelectrics and materials in ferroelectric, random access memory (FeRAM) applications (Fig. 1). Recently it has been shown that ferroelectricity can persist in exfoliated Aurivillius phase nano-flakes with thicknesses of only 2.4 nm, which equates to one-half of the normal crystal unit cell (2).

Defining features of the Aurivillius phase materials are their established ferroelectricity and reversible spontaneous polarisation. The origin of this ferroelectric property is due to the non-centrosymmetric tilt of the perovskite octahedra. Predominantly, this polarisation is in the *a/b*-axis direction. As is discussed in Section III., some members of the Aurivillius family may also possess a smaller polarisation in the *c*-axis direction.

The chemical composition of these materials can vary considerably as different atoms can be accommodated at the *A* and *B* sites of the perovskite blocks. As presented in Section IV., substitution at the *A* and *B* sites has been used to change the piezoelectric coefficient, fatigue resistance, morphology, conductivity and resistivity. Insertion of magnetic ions at the *B* site has been shown to induce ferromagnetic or antiferromagnetic behaviour thus creating a genuine room temperature multiferroic material (3), as described in Section VI. Section V. reviews how optical properties, such as band gap, have also been adjusted through atomic substitution for potential photocatalytic, photovoltaic and photoluminescence applications.

Figure 1: Scientific publications per year

Increasing number of scientific publications on Aurivillius phase materials. Image generated from data taken from Web of Science database, August 2019.

The role of physical factors such as growth on template substrates and how the presence of out-of-phase boundary defects (4) affect distribution of cations within the Aurivillius is an emerging area of study and is discussed in Section VIII. Physical strain imparted by the substrate offers another means of tailoring the ferroelectric, ferromagnetic and optical behaviour of Aurivillius materials (5).

The Aurivillius layered oxides are versatile group of materials and already have uses in commercial FeRAM devices (6, 7). As will be discussed in greater detail in the following review the Aurivillius materials are being examined as high temperature piezoelectrics, fatigue free ferroelectrics and photocatalytic materials for the degradation of organic compounds. Of particular interest to the authors is the development of phase pure multiferroic materials and a case study on the development of a genuine room temperature multiferroic is presented (Sec VII). Also highlighted are the challenges in determining the phase purity of such materials and a statistical methodology for assigning a confidence level to a materials phase purity is detailed (Sec VII).

II. Aurivillius phase structure

II.1. Aurivillius phase structure

The Aurivillius homologous series of compounds are a type of layered perovskite material that consists of a number of perovskite blocks ($mABX_3$) separated by a fluorite-like $[\text{Bi}_2\text{O}_2]^{2+}$ intermediate layer. The number of perovskite blocks (m) between the fluorite layers can range from 1-9 and the structure is described by the general formula $A_{m-1}B_mX_{3m+1}$. For example, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ have $m = 3, 4$ and 5 perovskite units respectively. Repeat units of perovskite blocks regularly interleave with the $[\text{Bi}_2\text{O}_2]^{2+}$ sheets along the c -axis direction. This creates a naturally nanostructured 2-dimensional layered material (Fig 2).

Figure 2: Aurivillius phase materials

(a) Bi_2WO_6 space group $A2/m$ (b) $\text{Bi}_3\text{TiNbO}_9$ space group $A21am$ and (c) $\text{Bi}_4\text{Ti}_3\text{O}_{15}$ space group $I4/mmm$. Images generated using VESTA (11).

A related layered perovskite material group is the Sillén-Aurivillius series of materials. These are a type of Aurivillius structure that contains a halide layer next to the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer. The general formula of the Sillén-Aurivillius interlayer can be described as $[\text{M}_2\text{O}_2]\text{Y}_z$, where $M = \text{Bi}^{3+}, \text{Pb}^{2+}$ etc., Y is a halide, e.g. F^- , Cl^- , Br^- , and $z = 1-3$ (8). The

Sillén-Aurivillius area of research is beyond the scope of this review. Other distinct families of layered perovskite materials include the Ruddleson – Popper and Dion – Jacobson structures. A variety of fabrication methods can be used to synthesise Aurivillius structures. These range from the relatively simple chemical solution deposition (CSD) and hydrothermal growth methods to chemical vapour deposition (CVD), pulsed laser deposition (9) and solid-state reactions, which require more specialised equipment. The fabrication method also influences the properties of the material and must be taken into account when approaching the design of a specific material. Further details on synthetic methods can be found within this review (10).

II.2. $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer

The fluorite-like $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer has an average thickness of 4.08 Å (9). It is paraelectric therefore does not retain polarisation when an electric field has been removed. The interlayer acts as an insulator and ferroelectricity in the Aurivillius phase materials tends to be much larger in the a/b-axis direction compared with the c-axis direction. Although the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer is generally considered to be inviolate, meaning its atoms are not easily substituted with different atoms (12), substitution at the Bi position in the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer with Pb (13, 14) and La (15) has been reported. A first principles calculation using density function theory of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ examined the theoretical effects of substitution at the Bi site of the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayers. Substitution of 6.25% of the Bi with isovalent atoms such as S, P and As was predicted to induce strong out-of-plane polarisation along the c-axis (16).

II.3. Perovskite structure

An ideal perovskite structure consists of a cube with the *A*-site atoms at the corner positions, the *B*-site atom at the body centre of the cube and *X* atoms at the face centre positions. As there are a range of atoms that can be accommodated at the *A* and *B* cation site positions, the stoichiometric composition of Aurivillius phase materials can vary widely. *X* is usually oxygen but several structures with fluorine have been fabricated (17). The versatility of stoichiometric composition allows the chemical properties of the material to be tuned using substitution. The atomic radius and valence of atoms determine what can be incorporated into the perovskite structure. Possible atoms for occupying the *A*-site include Na^{1+} , K^{1+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} and Bi^{3+} and at the *B*-site; Fe^{3+} , Ti^{4+} , Nb^{5+} , W^{6+} , Ta^{5+} and Cr^{3+} . More generally, the *A*-site is occupied by a large 12 coordinate cation and the *B*-site a smaller 6 coordinate octahedral cation.

The Goldschmidt tolerance factor (Eq 1) provides a measure of the stability or distortion of the perovskite unit based on the atomic radii (18). An ideal cubic

perovskite structure has a t value of 1. When B - X bonds are compressed, and the A - X bonds are expanded then $t < 1$. As t decreases, the tilt of the octahedral unit increases to accommodate this strain (18). This tilting provides the non-centrosymmetric geometry necessary for ferroelectric behaviour. For Aurivillius phase materials a tolerance factor below 0.985 is necessary for octahedral tilting (19). Ferroelectric behaviour will be discussed in greater detail in Section III.

Armstrong *et al.* (20) proposed a range of ions with atomic radii between 0.58 and 0.645 Å that can be accommodated at the B -site. As the perovskite blocks are constrained between the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayers, the upper limits of atomic radii that can be accommodated within the Aurivillius structure is actually lower than that of an independent perovskite block. They also proposed that if larger atoms such as Zr^{4+} (0.72 Å) were incorporated, the lattice mismatch between the perovskite blocks and the interlayer would be too great and the structure would break down (20). However, recently Zr has been incorporated into the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Aurivillius structure (21).

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)}$$

Equation 1: Tolerance factor

t = tolerance factor, r_A , r_B and r_O are the average effective ionic radii relative to oxygen of the A-site cation, and B-site cation and oxygen anion respectively (22).

Due to the formal charge of 2+ on the Bi_2O_2 interlayer ($[\text{Bi}_2\text{O}_2]^{2+}$), an overall formal charge of $[\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}]^{2-}$ must be maintained on the perovskite blocks. The valence of atoms is particularly important when substituting atoms into the Aurivillius structure and is further discussed in Section IV.

II.4. Homologous series

By increasing the number of perovskite blocks (m) which are interleaved between the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayers, a homologous series of Aurivillius compounds is achieved, with structures having m values ranging from one to nine so far reported in the literature (23). As the thickness of the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer is 4.08 Å (f) and the average thickness of the perovskite blocks tends to be ≈ 4 Å (p) then the thickness of a unit cell along the growth axis (c) can be estimated using the relationship $c/2 = f + h$, where $h = m \cdot p$ (24). The properties of these Aurivillius materials change systematically with increasing m . For example, with the homologous series $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ ($m = 3$ to 9), the thermal stability was found to decrease with increasing m (24).

It is also possible to get non-integer values of m due to the presence of varying numbers of perovskite end members within a sample. Mixed phase super-lattice materials are also possible. Materials that have alternating $m=2$ and $m=3$ phases present within a sample have an average m value of 2.5. As examples, $(\text{Bi}_3\text{TiNbO}_9)_2(\text{Bi}_4\text{Ti}_3\text{O}_{12})$ (25) or $(\text{Bi}_3\text{TiNbO}_9)_1(\text{Bi}_4\text{Ti}_3\text{O}_{12})_2$ (26) consist of alternating $m=2$ and $m=3$ perovskite blocks. Alternating $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ $m=3$ and $\text{Bi}_3\text{TiNbO}_9$ $m=2$ along the c -axis was found to increase the remanent polarisation ($P_r = 20.1 \mu\text{C}/\text{cm}^2$) of the composite material compared to individual $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ $m=3$ ($P_r \approx 16 \mu\text{C}/\text{cm}^2$) or $\text{Bi}_3\text{TiNbO}_9$ $m=2$ ($P_r \approx 11 \mu\text{C}/\text{cm}^2$) materials (27). More complex intergrowth Aurivillius compounds, such as $(\text{Bi}_3\text{TiNbO}_9)_1(\text{Bi}_4\text{Ti}_3\text{O}_{12})_2$ which grow in a repeating -2,3,3- pattern of m , have also been fabricated (28).

Minor c -axis polarisation occurs in Aurivillius structures which have an odd number of perovskite blocks (12). Interesting properties can be observed due to stacking faults of different m phases. These lead to out-of-phase-boundary (OPB) defects, which will be discussed in greater detail later in this work in Section VIII.

II.5. Phase transitions

The paraelectric high temperature phase adopted by Aurivillius compounds is usually the $I4/mmm$ tetragonal symmetry phase. An exception to this is Bi_2WO_6 , which adopts the $A2/m$ monoclinic phase at high temperatures (950°C). Bi_2WO_6 has an intermediate transition phase, $B2cb$ (670°C) and the ferroelectric ground state phase is $P21ab$ (29).

At lower temperatures most Aurivillius compounds undergo a phase transition to a ferroelectric phase either orthorhombic or monoclinic (30). Initial work on determining the ferroelectric phase of the $\text{Bi}_5\text{Ti}_3\text{Fe}_1\text{O}_{15}$ Aurivillius material proposed the space group $Fmm2$ through a transition phase $Fmmm$ (31). If this Aurivillius phase material was of the $Fmmm$ space group, this would mean that the stacking axis would be along the a -axis direction. However, later work showed structures with an even number of perovskite blocks, such as $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (Fig 3) and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ($m=4$) or $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Sr}_{0.85}\text{Bi}_{2.1}\text{Ta}_2\text{O}_9$ ($m=2$), transition from the $I4/mmm$ paraelectric phase ($\text{Sr}_{0.85}\text{Bi}_{2.1}\text{Ta}_2\text{O}_9$, T_C 550°C), through an intermediate $Amam$ phase ($\text{Sr}_{0.85}\text{Bi}_{2.1}\text{Ta}_2\text{O}_9$ T_C 375°C), to the $A21am$ space group (32, 33). Despite this, the $Fmm2$ space group is still sometimes reported (34, 35). Aurivillius structures with an odd number of perovskite blocks such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$) transition from the $I4/mmm$ phase to the orthorhombic $B2cb$ phase T_C 676°C (12, 36). However, in the case of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, a further transition from $B2cb$ to a lower symmetry phase, the monoclinic $B1a1$ phase, has been confirmed as the room temperature phase (37, 38). $\text{SrBi}_2\text{Nb}_2\text{O}_9$ ($m=2$) was shown to transition directly from $I4/mmm$ to $A21a$ (T_C 440°C) (39, 40).

Figure 3: Paraelectric and ferroelectric phase

Images of the Aurivillius material $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ in its (a) paraelectric $I4/mmm$ phase and (b) ferroelectric $A21am$ phase. Images generated using VESTA (11).

An abrupt lattice expansion of the $I4/mmm$ phase of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ and $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ at high temperatures, (1110K and 1021K respectively) has been reported (41). Superlattice structures such as $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-SrBi}_4\text{Ti}_4\text{O}_{15}$ ($m=3\text{-}4$) (42) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-Bi}_5\text{Ti}_3\text{Fe}_1\text{O}_{15}$ ($m=3\text{-}4$) were assigned to the space group $P2_{1am}$ (43).

III. Ferroelectric Behaviour of Aurivillius Phases

Ferroelectricity involves the spontaneous alignment of electrical dipoles in the presence of an applied electric field. This alignment is maintained in the absence of an applied field and the orientation of polarisation can be switched by applying an electric field in that direction. The adoption of non-centrosymmetric phases by Aurivillius materials at lower temperatures provides the break in symmetry required to enable a net dipole moment so that ferroelectricity can occur. The creation of a non-centrosymmetric structure is stabilised through the hybridisation of the *B*-site orbitals d^0 (commonly Ti 3d) and O 2p orbitals. This hybridisation creates a double well potential which stabilises the structure. *Ab initio* calculations have been used to

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investigate the energy level degeneracy of the Ti 3d e_g orbitals in the ferroelectric phase of Aurivillius materials having TiO_6 perovskites units (44). In the ferroelectric phase, the Ti 3d_z orbital is of lower energy than the 3d_x and 3d_y orbital. This distortion to remove degeneracy in either the t_{2g} or e_g orbitals is known as Jahn-Teller deformation (44). In the cubic phase, with all axes having equal lengths, this degeneracy is restored.

The ferroelectric properties in Aurivillius phase materials are anisotropic and should be preferably studied in single crystals. However, there is a lack of such analysis currently due to the difficulties in growing large single crystals on conductive bottom electrodes. Therefore, epitaxial thin films provide insights to the anisotropic nature of ferroelectricity in Aurivillius compounds. Growth on epitaxial substrates such as (001) and (110) La-substituted SrTiO_3 (43) and (100) SrTiO_3 , (110) SrTiO_3 , (111) SrTiO_3 and (101) TiO_2 (45) provide information of the direction of polarisation in these thin films.

The origin of the ferroelectric behaviour arises due to the displacement of the *A* and *B*-site atoms along the *a*-axis and a tilt of the BO_6 octahedral unit around the *a*-axis. However, even and odd *m*-valued structures lead to different rotations based on symmetry differences between even and odd *m* numbers (37). The BO_6 octahedra receive strain energy from the bismuth oxide layer, caused by bond formation between an apex oxygen of the perovskite layer and the Bi ion of the $[\text{Bi}_2\text{O}_2]^{2+}$ layer. In structures with even *m* values, this strain is minimised as they retain mirror symmetry perpendicular to the *c*-axis. Retention of this mirror symmetry results in cancellation of polarization across the *c*-plane. The spontaneous reversible polarisation occurs along the *a*(*b*)-axis of the perovskite units, parallel to the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer and the stacking axis. In Aurivillius phase materials with an odd number of perovskite blocks, a break in symmetry along the *c*-axis occurs. It is not possible to retain mirror symmetry since this would cause deformation of the BO_6 octahedra. This non-centrosymmetric axis allows minor polarisation to occur along the *c*-axis. This polarisation tends to be much lower than the primary polarisation along the *a*(*b*)-axis direction (45). In even-numbered perovskite blocks, the presence of a mirror plane results in cancellation of the polarisation along the *c*-axis.

The displacement of cations in the perovskite blocks is responsible for this polarisation. This allows a small degree of freedom for the *B*-site atoms to move out of plane but at a much lower magnitude than with in-plane polarisation (46). The extent of the polarisation can be altered through substitution of different cations at the *A* and *B*-sites (47, 48). Much effort then has been spent on increasing the polarisation value through substitution of suitable atoms at the *A* and *B*-sites of the perovskite unit. This can affect the polarisation value by increasing the tilt of the perovskite unit, thereby increasing distortion and results in the polarisation increasing directionally. Substitution at the *A*-site of the Aurivillius $\text{SrBi}_2\text{Ta}_2\text{O}_9$ material involved the substitution of Sr^{2+} with

Bi^{3+} which resulted in greater structural distortion and higher polarisation along the a -axis and a higher Curie temperature compared with the parent sample (49). B -site titanium has been substituted in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with Nb (50), V (51) and Yb (52) and with Nb in $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (53).

The temperature at which the phase transition occurs between the paraelectric and ferroelectric phase is known as the Curie temperature (T_c). This temperature is characteristic for each material. The Aurivillius series in general exhibits a relatively large in-plane spontaneous polarisation (0.4 Cm^{-2}) and have high Curie temperatures ($T_c > 500^\circ\text{C}$) (30). A linear relationship is observed between the degree of displacement of the B -site atom and a corresponding increase in T_c (19, 49). As mentioned before (Section II.3), the tolerance factor is a measure of the tilt of the perovskite unit. For Aurivillius materials, with a decrease of tolerance factor ($t < 1$), a corresponding increase in T_c is observed (22). The phase transition from paraelectric to ferroelectric may sometimes pass through intermediate phases, which can exhibit ferroelectric (29) or antiferroelectric (54) behaviour.

The $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer is generally paraelectric and does not contribute to the polarisation of the Aurivillius phase materials. In fact, the displacement of neighbouring atoms in the perovskite units is hindered by the interlayer and this causes strain on the adjacent perovskite blocks. The effect of this strain is diminished with increasing numbers of perovskite units (19). Interestingly, the strain caused by a lattice mismatch between alternating $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ units in the superlattice structure $\text{Bi}_4\text{Ti}_3\text{O}_{12}\text{-SrBi}_4\text{Ti}_4\text{O}_{15}$ induces displacement of a Bi atom from the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer along the a -axis. This displacement contributed to the polarisation value ($2P_r = 30 \mu\text{C}/\text{cm}^2$) of the composite Aurivillius material. The resulting polarisation was almost double what was measured for individual $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ Aurivillius material (42).

IV. Cation Substitution of Aurivillius Phases

IV.1. Cation Substitution of Aurivillius Phases

The chemical composition within the Aurivillius family can vary enormously; however, with only a small change in the concentration of a particular atom, a drastic impact on the properties of the materials is observed. Having already mentioned that it is generally accepted that the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer is inviolate, this section will focus on a much larger area of research, the substitution of atoms at the A and B -sites within the perovskite units. Substitution can affect the properties of the Aurivillius phase material by altering the physical structure and/or its electrical environment. Below we shall highlight examples of studies that have been undertaken to tailor the properties of

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Aurivillius phase materials towards target applications. This is by no means an exhaustive list but will serve to highlight the versatility of the Aurivillius structure.

The resistivity and conductivity of the Aurivillius phase materials is dominated by the role of oxygen vacancies (55). Examination of the dependence of conductivity on the partial pressure of oxygen in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Aurivillius materials showed that ionic p -type conduction occurred along the a -axis and p -type conduction occurred along the c -axis (56). The conductivity of bismuth layered perovskite systems was found to be p -type at low temperatures due to the formation of holes (51). Bismuth is volatile, particularly at the relatively high temperatures required for synthesis of Aurivillius phases, which results in bismuth vacancies as bismuth migrates through the samples. This leads to an increase in the concentration of associated oxygen vacancies with increasing temperature. This results in a higher conductivity and leakage currents at higher temperatures. The higher conductivity is a limiting factor for the use of Aurivillius phase materials in high temperature applications, as it is energetically more difficult to switch polarisation. Oxygen vacancies reside preferentially in the perovskite units and not within the $[\text{Bi}_2\text{O}_2]^{2+}$ interlayer (51). Co-substitution of W^{6+} and $\text{Mn}^{3+/2+}$ for Ti^{4+} in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ improved the resistivity of the material (57). Two different mechanisms, at high and low temperatures, were investigated to explain this improvement. At high temperatures ($>300^\circ\text{C}$), donor substitution of W^{6+} reduced the density of oxygen vacancies.

Eq 2: Kröger–Vink notation

Kröger–Vink notation showing [a] substitution of an electron donor [b] substitution of an electron acceptor, [c] the neutralisation of intrinsic oxygen vacancies and [d] elimination of a hole through oxidation state change.

The introduction of electron donor atoms, produces an excess of electrons in the material which can neutralise oxygen vacancies, thereby decreasing the conductivity of the material (Eq 2 [a] and [c]). At low temperatures ($<300^\circ\text{C}$), Mn underwent a change in oxidation state from 2+ to 3+ through the absorption of a hole (Eq 2 [d]), thereby decreasing the concentration of charge carriers in the material (57).

IV.2. Piezoelectric coefficients

Aurivillius materials tend to have large Curie temperatures (<500°C) which makes them suitable for high temperature piezoelectric applications, such as aircraft, aerospace or nuclear industries. However, they also tend to have low d_{33} piezoelectric coefficients, due to the structure's anisotropy, which would limit their effectiveness for these practical applications. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has a relatively low d_{33} piezoelectric coefficient of 3.5 pC/N. The substitution of Nb^{5+} and W^{6+} for Ti^{4+} to form the $\text{Bi}_4\text{Ti}_{2.9}\text{W}_{0.05}\text{Nb}_{0.05}\text{O}_{12}$ material resulted in an increase in the d_{33} to 22.8 pC/N. Substitution involving the replacement of atoms with those of a higher oxidation state (Ti^{4+} substituted with Nb^{5+} and W^{6+}) was reported to improve the piezoelectric coefficient by trapping oxygen vacancies (Eq 2 a,c) and thereby increasing resistivity by reducing the number of charge carriers (58). Replacing Nb^{5+} with W^{6+} at the *B*-site of the Aurivillius structure $\text{Bi}_{2.93}\text{Ce}_{0.07}\text{TiNb}_{1-x}\text{W}_x\text{O}_9$ ($x = 0 - 0.06$) resulted in a maximum d_{33} of 19.2 pC/N at $x = 0.02$ compared to a d_{33} value of 7 pC/N for the $x = 0$ material. The $x = 0.02$ material maintained 92 % of this improved piezoelectric coefficient value at 700°C (59). The increase in d_{33} was attributed to greater structural distortions on substitution. W^{6+} has a smaller atomic radius than Nb^{5+} , therefore its inclusion increased the octahedral tilt angle of the perovskite unit. As concentrations of tungsten greater than $x = 0.02$ were added to the structure, there was a reduction in the piezoelectric coefficient due to the improved symmetry of the *B*-O bonds of the octahedron as more W^{6+} is substituted (59).

A range of elements have been used to modify piezoelectric behaviour of Aurivillius phase materials. As examples, $\text{Li}^+/\text{Ce}^{3+}$ A-site substitution and Sr^{3+} *B*-site co-substitution of $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Ta}_2\text{O}_9$ (60) and a range of ceramics based on $\text{Bi}_3\text{TiNbO}_9$ were modified with Na, Ca, Sc, W, Mo (61) and Ce (62).

IV.3. Fatigue resistance

The Aurivillius phase materials are generally regarded as having high fatigue strengths. A fatigue breakdown after $\sim 10^6$ switching cycles has been attributed to either the development of a non-switching layer at the ferroelectric - electrode interface (63) or due to the pinning of domains by internal stresses within the material (64). In Aurivillius phase materials, oxygen vacancies affect the switching performance over time by pinning domain walls. Substitution at the A-site with La was found to improve the fatigue properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Aurivillius material. It was proposed that this could be due to the lattice distortion caused by atomic radii differences. Alternatively, this could be attributed to the suppression of Bi volatility, improving the stability of the material and suppressing the formation of oxygen vacancies (65). An example of substitution at the *B*-site was reported for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ co-substituted with Cu^{2+} and Nb^{5+} in place of Ti to produce the system $\text{Bi}_4\text{Ti}_{3-x}(\text{Cu}_{1/3}\text{Nb}_{2/3})_x\text{O}_{12}$, where $x = 0, 0.005, 0.01$,

0.015, 0.02, 0.03, 0.04 and 0.05. At $x = 0.015$, the material showed a marked increase in d_{33} , an increase in resistivity and improved fatigue resistance. This was attributed to the suppression of oxygen vacancies by the substituted atoms (66). An increase in resistivity observed for materials with $x > 0.03$ was proposed to be due to a change to an n -type conduction system due to the increased donor substitution of Nb^{5+} (66).

IV.4. Morphology

The Aurivillius phase materials can adopt a range of different morphologies. This is often dependent on the fabrication method, substrate effects and the chemical composition of the material. Small changes to the chemical composition have a clear impact on the morphology of grains. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ forms plate like grains but the introduction of small concentrations of Nb resulted in the growth of more disordered grains. La substitution resulted in a 'spherical staking like form' (67). A comparison between $\text{Bi}_4\text{Ti}_{3-x}\text{W}_x\text{O}_{12}$ fabricated by conventional mixing oxides and co-precipitation methods found that the mixing solid method produced larger plate-like grains with a larger electrical conductivity, corresponding to materials having a larger aspect ratio (68).

V. Optical Properties of Aurivillius Phases

V.1. Photovoltaic properties

Light induced excitation of electrons in perovskite structures has been of increased interest for photovoltaic applications. The substitution of Ho into $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($m=4$) improved the fatigue resistance of the photovoltaic material (69). A-site substitution of neodymium for bismuth in $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($m=4$) demonstrated differences between the randomly orientated ceramic and a c-axis orientated material. The randomly orientated material had a larger photocurrent J_{sc} and a smaller photovoltage V_{oc} , compared to the c-axis orientated material (70). Substitution of transition metals, such as Fe/Ni/Co co-substitution of $\text{Bi}_6\text{Ti}_3\text{Fe}_{2-x}\text{Co}_{x/2}\text{Ni}_{x/2}\text{O}_{18}$ ($m=5$), narrows the band gap, allowing more of the visible spectrum to be utilised (71).

V.2. Photocatalytic properties

Hybridisation of orbitals, which stabilises ferroelectric distortions, also improves the separation of charge carriers in the material. The absorption of light by a material can generate charge separation and the formation of an electron-hole pair. By improving the charge transport through the material, the lifetime of these charge carries can be extended by reducing charge recombinations. The lifetime of this charge separation is

an important factor in potential photocatalytic materials. The presence of charge carriers at the surface of the material can be utilized in redox reactions. A comparative study between hydrothermal and solid-state fabrication of $\text{Bi}_3\text{Fe}_{0.5}\text{Nb}_{1.5}\text{O}_9$ highlighted the effects of morphology and crystal ordering on the photo-degradation capabilities of the materials. The hydrothermal method was found to produce a material that was more effective at the photodegradation of rhodamine B (RhB) and salicylic acid. This result took into consideration the difference in specific surface area between the materials. The Aurivillius phase materials grown using the hydrothermal method took the form of nanosheets with the (001) and (110) facets exposed at the surface. These exposed areas align with the polarisation directions along the c and a/b-axis respectively. The spontaneous polarisation along these axes may have helped charge separation. Absorption of light enabled charge separation into negative electron and positive hole charge carriers. It was found that photo-degradation of the dye was due to positive charge carriers in the material. This indicated that the positive charge carriers migrate to the surface of the materials where a hole driven oxidation reaction occurs (72).

V.3. Photoluminescence characteristics

The absorption of energy can promote an electron from its low energy ground state to a higher energy excited state. When the electron drops down from its excited state, this is accompanied by the emission of a photon of the same energy as the difference between the excited state and ground state energy levels. Transitions between energy levels in Sm^{3+} produce light with energies corresponding to the orange region of the solar spectrum. The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Aurivillius phase material was found to be a suitable host for Sm^{3+} and a series of thin films were prepared. With $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_3\text{O}_{12}$ having $x=0.14$, a maximum intensity and a photoluminescence lifetime of ≈ 0.8 ms was achieved (73). Similarly, Er^{3+} substitution in Aurivillius phase materials is an area of interest in developing photoluminescence materials and a strong up-conversion photoluminescence was observed in $\text{Bi}_{4-x}\text{Er}_x\text{Ti}_3\text{O}_{12}$ with $x = 0.2$ (74).

VI. Aurivillius magnetoelectric multiferroics

VI.1. Aurivillius magnetoelectric multiferroics

Multiferroic materials exhibit both ferroelectric and ferromagnetic behaviour in the same phase (75, 76). Multiferroic materials are of increasing interest due to their potential applications. Two of the main applications of interest are multiferroic tunnel junctions (MFTJs) (77) and magnetoelectric-RAM applications (78). MFTJs consist of two asymmetric oxide and/or metal electrodes separated by an ultra-thin multiferroic barrier layer. This, in theory, allows the combination of electroresistance and

magnetoresistance resulting in a four-state memory effect. Multiferroics may also show coupling between the two 'ferro' behaviours and thus be termed magnetoelectric multiferroics. This raises the possibility of controlling the magnetic polarisation by applying an electric field. Magnetoelectric memory storage devices which can be 'electrically written and magnetically read' are attractive as they provide stable data storage with higher data storage densities and with lower power consumption (10^{-18} J per switch) (79).

Despite the potential benefits and increasing research attention, multiferroic materials are rare due to the competing electronic structure requirements necessary for atoms that drive ferroelectric and ferromagnetic behaviour. Conventionally, ferroelectricity requires empty *d*-orbitals for hybridisation, while magnetic coupling occurs between neighbouring magnetic ions with partially filled *d* orbitals (76, 80). Typically, ferroelectric and ferromagnetic behaviour arises from different atoms. BiFeO₃ is a multiferroic with a primarily antiferromagnetic interaction between Fe³⁺ ions at room temperature and ferroelectricity arising from the Bi-O interactions (81).

The Aurivillius phase materials provided a versatile scaffold that can accommodate ions with both empty and partially filled orbitals. Substitution of magnetic ions, usually at the *B*-site of the perovskite unit, but also *A*-site substitution (e.g. lanthanides), is being examined to develop single phase multiferroic materials. Transition metal ions are commonly substituted at the *B*-site. The most common starting materials for developing multiferroic Aurivillius materials are Bi₄Ti₃O₁₂ and Bi₅Ti₃FeO₁₈ to which ions such as Fe, Nb, Co, Tb, Mn, Sm, Ni, Gd, Cr, W and Cr are substituted at the *B*-site and La, Sr, Gd, Dy and Tb at the *A*-site. Candidate multiferroic materials, such as Bi₅Ti₃FeO₁₅ and Bi₆Ti₃Fe₂O₁₈, can be thought of as the Aurivillius material Bi₄Ti₃O₁₂ with one and two BiFeO₃ perovskite units respectively inserted into the structure. The main challenges to overcome when developing an Aurivillius multiferroic include the achievement of high quality, single-phase materials, achieving a sufficiently large magnetic response and the ability to perform at room temperature.

VI.2. Single phase multiferroics

A serious issue in examining potential multiferroic materials is establishing that the material is indeed phase-pure and that any magnetic signal observed is due to the successful incorporation of magnetic ions into the crystal structure and not due to the presence of magnetically active second phase impurities that may segregate out into the sample matrix (82). This is not a trivial task as very small impurity volumes can still be responsible for the overall magnetic response of a sample. For example, Tb_{0.90}Bi_{5.1}Fe₂Ti₃O₁₈ was observed to have a small (<0.05 emu) magnetic moment at 2K but detailed microstructure analysis showed that 4 vol.% of secondary phase Fe_xTb_yO_z was responsible for this magnetic response (83). Similarly the magnetic response (804

memu/g) in $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{15}$ was attributed to a 3.95 vol.% Fe/Co-rich spinel impurity phase (84). This research illustrates that detailed microstructure analysis is required before a material can be declared free from interfering impurities and denoted a single-phase multiferroic.

Another challenge in this area of research is the reliability of reported magnetic responses. Polarized neutron reflectivity measurements (PNR) of thin film multiferroics found a significant decrease in the measured magnetisation compared to the results obtained by superconducting quantum interference device (SQUID). PNR can fit the magnetizations from the depth-dependent measurements of thin films and exclude external sources of magnetic moment. Measurements of the room temperature multiferroic $\text{LaBi}_5\text{FeCoTi}_3\text{O}_{18}$ produced a value of $0.016 \pm 0.027 \mu\text{B/Fe-Co}$ with PNR, however a value of $0.4 \mu\text{B/Fe-Co}$ was measured using SQUID magnetization (85). This is an order of magnitude difference and highlights the need for rigorous analysis when reporting magnetisation values for multiferroic materials.

VI.3. Magnetic behaviour in Aurivillius phase materials

When discussing multiferroic materials, both antiferromagnetic and ferromagnetic behaviour tend to be included in the term and both have been observed in Aurivillius materials. Magnetic coupling arises from different mechanisms, including super-exchange and the double-exchange mechanisms (86). The super-exchange mechanism involves an electron transfer through an intermediate non-magnetic atom. In the Aurivillius materials this is nearly always between the $3d$ orbital of transition metals (eg. Ti) and $2p$ orbital of oxygen (86). According to the Goodenough-Kanamori rule, super-exchange interactions are antiferromagnetic when virtual electron transfer takes place between overlapping orbitals that are each half-filled, for example between the e_g orbitals in high-spin Fe(III). In antiferromagnetic materials, neighbouring metal ions couple with their spins antiparallel. The antiparallel spins result in a net polarisation of zero at zero applied field. Common magnetic interactions in Aurivillius phase materials such as $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ or $\text{Mn}^{3+}\text{-O-Mn}^{3+}$ are responsible for antiferromagnetism. Alternatively, the Goodenough-Kanamori rule predicts that super-exchange interactions are strong and ferromagnetic when virtual electron transfer takes place from a half-filled orbital to an empty orbital, for example between a half-filled e_g orbital in high-spin Fe(III) and an empty e_g orbital in low-spin Mn(III), or in Mn(IV) where the e_g orbitals are always empty regardless of the extent of the octahedral splitting. In ferromagnetic materials, the electron spins of each of the atoms couple strongly together to form a resultant magnetic moment in an applied magnetic field. When the magnetic field is then removed, the magnetization does not return to its original value unless heated to the ferromagnetic Curie point temperature.

The double-exchange mechanism has important implications for whether materials are ferromagnetic, antiferromagnetic or whether they exhibit spiral magnetism. Here electrons are delocalised between ions with different oxidation states, such as $\text{Mn}^{3+}(d^4)\text{-O-Mn}^{4+}(d^3)$. This is a two-step process and the electrons are delocalised along the M-O-M bond. As changes in spin direction of electrons are not allowed (Hund's rule), neighbouring magnetic ions must retain their spin for the double-exchange mechanism to occur. The parallel alignment of spins in a material produces a ferromagnetic alignment of neighbouring ions and a net magnetic polarisation at zero applied field (86).

The Dzyaloshinskii–Moriya (D-M) interaction or antisymmetric exchange is responsible for weak ferromagnetism in antiferromagnetic ordered systems. It involves spin-canting leading to a net magnetisation (87). Compounds of $\text{DyBi}_5\text{Fe}_2\text{Ti}_3\text{O}_{18}$ exhibited competition between ferromagnetic and antiferromagnetic behaviour with ferromagnetic behaviour predominating at low temperatures (88). The Aurivillius materials are highly anisotropic and this affects the magnetisation properties. Magnetic measurements of the $x=0.6$ of $\text{Bi}_7\text{Fe}_{3-x}\text{Co}_x\text{Ti}_3\text{O}_{21}$ sample, for example, were M_R 1.50 emu/g parallel to the c-axis and M_R 1.17 emu/g perpendicular to the c-axis. This magnetic anisotropy was exacerbated with increasing number of perovskite blocks (89).

As shown, the oxidation state of the magnetic ions is important for the type of magnetic behaviour that occurs. Variable oxidation states can occur within the ions in Aurivillius phase materials. The formation of oxygen vacancies during high temperature annealing is accommodated by the release of electrons which can be taken up by atoms. A detailed study of the electronic structure of $\text{Bi}_6\text{Fe}_2\text{Ti}_3\text{O}_{18}$, $\text{Bi}_6\text{FeCoTi}_3\text{O}_{18}$, and $\text{LaBi}_5\text{FeCoTi}_3\text{O}_{18}$ Aurivillius materials was performed using resonant inelastic x-ray scattering (RIXS) and near-edge soft x-ray absorption (XAS). It was found that iron existed in the 3+ oxidation state, while cobalt existed predominantly in the 2+ oxidation state, although there was a small contribution from the cobalt 3+ oxidation state also (90). Whereas in $\text{Bi}_4\text{SmFeTi}_3\text{O}_{15}$ thin films, both Fe^{2+} and Fe^{3+} were confirmed with both X-ray photoelectron spectra and dielectric relaxation spectra (91). Due to the variable oxidation states of ions and the possibility of D-M interactions, pinpointing the origins of an observed magnetic signal is not trivial and more than one mechanism may be occurring in the material (88).

VI.4. Magnetic percolation

Magnetic coupling requires close proximity between the magnetic ions. To increase the probability that magnetic ions will be near-neighbours or next near-neighbours, two approaches are considered. The first is to increase the concentration of magnetic ions in the material (92). This will naturally increase the probability of ions being closer

together. The threshold for magnetic percolation in a 3-D lattice is 31% for nearest neighbour magnetic interactions (strong magnetic coupling) and 14% when considering both next nearest neighbour (weak magnetic coupling) and nearest neighbour interactions (93). However, increased concentrations of magnetic ions, which are often of a different valence and atomic radius, could potentially lead to structural instability and the formation of secondary phases. The substitution of magnetic ions may also affect other properties of the material such as Curie temperature, resistivity or fatigue behaviour. Methods such as aliovalent substitution have been shown to be effective in increasing the magnetic ion concentration. Aliovalent substitution involves co-substitution of two atoms, one with a higher oxidation state and one with a lower oxidation state than the atom that is being removed. For example, removing $2X^{3+}$ and inserting Y^{4+} and Z^{2+} instead. This maintains the electro-neutrality of the material as opposed to donor or acceptor substitution. This has been shown to be an effective method for increasing the content of magnetic atoms in the Aurivillius structure. Replacing Ti^{4+} with Fe^{3+} and Nb^{5+} allowed increased Fe^{3+} to be successfully incorporated into the $Bi_5Ti_3Fe_1O_{15}$ structure before impurity phases were detected (94). The Aurivillius material $Bi_{5-x}Th_xFe_{1+x}Ti_{3-x}O_{15}$ ($x = 1/3$) involved aliovalent substitution at the A-site with Th^{4+} and at the B-Site with Fe^{3+} (95).

The second approach is to engineer the Aurivillius phase material so that the substituting atoms preferentially occupy sites that put them in closer proximity to each other. There is experimental evidence that such site preference does occur naturally in these systems and is discussed further in Section VIII.

VI.5. Room temperature multiferroics

The ability to operate at room temperature is obviously preferred for practical applications, however the development of a genuine room temperature multiferroic is challenging. Magnetic behaviour arises from the alignment of electron spins orientated in the same direction and this is energetically favourable compared to a random orientation of electron spins. However, above a certain temperature, the thermal energy (kT) value is large enough to make the random orientation more favourable. This is the Néel temperature above which the magnetic behaviour is lost. Some room temperature multiferroics that have been reported include $Bi_6Ti_{2.8}Fe_{1.52}Mn_{0.68}O_{18}$ thin films (3) and $Bi_5Fe_{0.9}Co_{0.1}Ti_3O_{15}$ single crystalline nanoplates (96).

VI.6. Recent publications

There are many recent reports of multiferroic Aurivillius phase materials but very few of these have detailed microscopic analysis which would rule out secondary impurity phases contributing to the observed magnetic response. Some of the more recent publications are mentioned below in order of increasing number of perovskite blocks.

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A ceramic $\text{Bi}_3\text{Nb}_{1.125}\text{Fe}_{0.0625}\text{Co}_{0.0625}\text{Ti}_{0.75}\text{O}_9$ ($m=2$) single phase material exhibited anti-ferromagnetic behaviour below 153K was fabricated. The magnetic behaviour was ascribed to a super-exchange interaction of $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ and $\text{Co}^{3+}\text{-O-Co}^{3+}$ (97).

High pressure sintering produced a denser $\text{Bi}_4\text{LaTi}_3\text{FeO}_{15}$ ceramic than sintering at atmospheric pressure (98). DFT computational studies of a room temperature multiferroic $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{2.5}\text{Nb}_{0.25}(\text{Fe}_{0.5}\text{Co}_{0.5})_{0.25}\text{O}_{12}$ ($m=3$) ceramic predicted three distinct magnetic transitions corresponding to coupling between $\text{Co}^{3+}\text{-O-Co}^{3+}$, $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ and $\text{Co}^{3+}\text{-O-Fe}^{3+}$. These three transitions were observed in the experimental results (99). Antiferromagnetic super exchange interactions between equivalent Fe (such as $\text{Fe}^{3+}\text{-O-Fe}^{3+}$) at room temperature was observed in $\text{SrBi}_3\text{Nb}_2\text{FeO}_{12}$ ($m=3$) (100). Weak ferromagnetism at room temperature in $\text{Bi}_4\text{Co}_x\text{Fe}_{2x}\text{Ti}_{3-3x}\text{O}_{12}$ ($x=0\text{-}0.4$) ($m=3$) was ascribed to DM canting spins. Possible magnetic interactions in this material include; $\text{Fe}^{3+}\text{-O-Fe}^{3+}$, $\text{Co}^{3+}\text{-O-Co}^{3+}$, $\text{Fe}^{3+}\text{-O-Co}^{3+}$, $\text{Fe}^{3+}\text{-O-Fe}^{2+}$, $\text{Co}^{3+}\text{-O-Co}^{2+}$, $\text{Fe}^{3+}\text{-O-Co}^{2+}$ and $\text{Co}^{3+}\text{-O-Fe}^{2+}$ (101).

A comparative analysis of La, Nd and Ho substituted $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ceramics attributed increased magnetic response to different atomic radii of substituted atoms and an associated increase in distortion of octahedral tilt (102). Substitution of Bi^{3+} ions by Gd^{3+} ions at A-sites of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ was found to be ineffective for inducing room-temperature magnetic behaviour as it decreased the degree of the octahedral tilt (103).

Nickel substitution in five layered Aurivillius materials found that substituting Ni existed in both the 3+ and 2+ oxidation states. Increased Ni^{2+} concentration, which has a larger atomic radius, contributed to a larger observed magnetic response (104, 105).

Studies on Aurivillius phase materials with $m>5$ are comparatively sparse but increasing attention is being directed at these materials. A series of Aurivillius materials were fabricated ($\text{Bi}_{m+1}\text{Fe}_m\text{-}_3\text{Ti}_3\text{O}_{3m+1}$ (BFT- m , $m = 6, 7, 8, 9$)) to examine the effects of increased number of perovskite blocks on the properties of the Aurivillius phase materials. As m increased, the magnetic response was found to increase due to the increase in lattice disorder and the increased probability of $\text{Fe}^{3+}\text{-O-Fe}^{3+}$ coupling interactions (106). The substitution of Co and Co/Sm into $\text{Bi}_7\text{Fe}_3\text{Ti}_3\text{O}_{21}$ ($m=6$) showed increased ferromagnetic response at room temperature, again attributed to increased D-M interactions due to increased octahedral distortion (107). Antiferromagnetic and weak ferromagnetism was observed in $\text{Bi}_7\text{Fe}_2\text{CrTi}_3\text{O}_{21}$ ($m=6$) ceramics (108). Ferromagnetism has been reported in epitaxial $\text{Bi}_9\text{Ti}_3\text{Fe}_5\text{O}_{27}$ ($m=8$) thin films grown on SrTiO_3 substrates. The small compressive strain exerted on the material by the substrate is thought to influence the D-M interactions (109).

Chemical solution deposition is a relatively inexpensive and simple method to fabricate Aurivillius thin film materials. Details of the optimisation of this deposition method to

prevent the formation of the secondary pyrochlore $\text{Bi}_2\text{Ti}_2\text{O}_7$ phase are provided in a publication on four layered Aurivillius phase thin films $\text{Bi}_5\text{Ti}_3(\text{Fe}_x\text{Mn}_{1-x})\text{O}_{15}$. These materials exhibited ferroelectric 180° polarisation switching (Fig 4). No magnetic signal was observed in these samples (110).

Figure 4: PFM Lithography

$\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_{15}$ Aurivillius phase material deposited on SiO_2 -Si substrate using chemical solution deposition. (a) topography, (b) out of plane PFM amplitude and (c) out of plane PFM lithography with an applied dc bias of 33 V. Reprinted with permission from Keeney et al. (110).

Further comparative studies on $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_{15}$ and $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{15}$ thin films fabricated with CSD were conducted. Again, no magnetic response was exhibited by the $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_{15}$ material but the $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{15}$ material exhibited a weak magnetic response (6.37 emu/cm^3) at room temperature. However, the presence of a secondary magnetic phase $\text{CoFe}_{2-x}\text{Ti}_x\text{O}_4$ was detected by detailed phase analysis using XRD, TEM and STEM-EDX. The percentage volume of impurities in the bulk was determined to be 3.95 %. This relatively low concentration was sufficient to explain the observed magnetic response and no magnetic response intrinsic to the $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{15}$ material was observed using X-ray magnetic circular dichroism photoemission electron microscopy (XMCD-PEEM) analysis (Fig 5) (84).

The room temperature multiferroic Aurivillius material $\text{Bi}_6\text{Ti}_{2.8}\text{Fe}_{1.52}\text{Mn}_{0.68}\text{O}_{18}$ ($m=5$) was successfully fabricated by both chemical solution depositions (CSD) (3) and liquid injection chemical vapour deposition (LI-CVD) (111). The ferroelectric and ferromagnetic properties were studied and magnetoelectric switching at room temperature was demonstrated in both the CSD and LI-CVD samples. The materials were extensively analysed to determine their phase purity. During these investigations a statistical analysis approach was developed to quantify a confidence level that secondary impurity phases were not present.

Figure 5: XMCD-PEEM imaging

$\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Mn}_{0.3}\text{O}_{15}$ and $\text{Bi}_5\text{Ti}_3\text{Fe}_{0.7}\text{Co}_{0.3}\text{O}_{15}$ thin films. The bright spots indicate the magnetic impurity phase Reprinted with permission from Keeney *et al.* (84).

It is recommended that such statistical analysis will become standard across the field. Further details are discussed in the Case Study in Section VII.

VII. Case Study

VII.1. $\text{Bi}_6\text{Ti}_x\text{Fe}_y\text{Mn}_z\text{O}_{18}$, a single-phase room temperature multiferroic system

Having surveyed the literature on multiferroic Aurivillius materials and having highlighted the concerns with regards to the importance of phase purity measurements, we will now present a case study of developments that have resulted in a very promising multiferroic material for practical applications. Keeney *et al.* (3) targeted the $m=5$ Aurivillius phase structure in order to increase the concentration of

magnetic ions (Fe and Mn) compared with the lower m phases. Initially samples were fabricated using CSD. Magnetic measurements of the $\text{Bi}_6\text{Ti}_{2.8}\text{Fe}_{1.52}\text{Mn}_{0.68}\text{O}_{18}$ (B6TFMO) thin films yielded a saturated magnetisation of $M_s = 0.74$ emu/g at 300K and coercivity of $H_c = 7$ mT. Magnetic-field-induced switching of both lateral and vertical ferroelectric domains was clearly demonstrated by piezoresponse force microscopy (PFM) measurements in the presence of an applied magnetic field (Fig 6). Extensive analysis was conducted to determine the phase purity of the material and only small amounts (0.1%) of a $\text{Mn}_{0.53}\text{Fe}_{0.47}\text{O}$ secondary phase were detected. This material is antiferromagnetic below 150 K and no other ferromagnetic or ferrimagnetic phases were detected. Microstructural analysis, coupled with the use of a statistical analysis of the data, concluded that ferromagnetism does not originate from second phase inclusions, with a confidence level of >99.5% (see section VII.1) and that multiferroicity is intrinsic to the Aurivillius phase (3).

This promising B6TFMO system was then targeted using a different deposition technique, liquid injection - chemical solution deposition (LI-CVD) (111). The results obtained from this method were even more promising as the magnetic response of $\text{Bi}_6\text{Ti}_{2.99}\text{Fe}_{1.46}\text{Mn}_{0.55}\text{O}_{18}$ prepared by LI-CVD was 35 times greater than the response obtained from the CSD grown films (24.25 emu/g, $H_c = 170$ Oe) (Fig 7). These thin film samples also clearly showed ferroelectric domain switching with an applied magnetic field (Fig 8). Some interesting features observed in these samples include the presence of both reversible and irreversible magnetoelectric switching. This is thought to be due to the orientation of the grains with respect to the magnetic field, with reversible magnetoelectric switching likely when crystallites are orientated parallel with the applied magnetic field direction. Note that reversible magnetoelectric switching is of interest for practical magnetoelectric device applications.

The increased magnetic response (24.25 emu/g), compared to the CSD sample (0.74 emu/g), was determined to be due to the improved deposition process.

Transition electron microscopy (TEM), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and scanning transmission spectroscopy-energy dispersive X-ray spectroscopy (STEM-EDX) are capable of nanometer resolution sample analysis.

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Figure 6: Ferroelectric domain switching

Ferroelectric domain switching in $\text{Bi}_6\text{Ti}_{2.8}\text{Fe}_{1.52}\text{Mn}_{0.68}\text{O}_{18}$ by an applied magnetic field. (a) topography, (c) lateral PFM amplitude and (e) lateral PFM phase under 0 mT (-1.9 Oe) H field and (b) topography, (d) lateral PFM amplitude and (f) lateral PFM phase under +250 mT (+2501 Oe) H field. Reprinted with permission from Keeney *et al.* (3).

However, these techniques are typically limited to a scan size of only several μm^2 . If impurities of only < 1 % of the material are present it is possible that they could be missed during a single analysis measurement.

Figure 7: Magnetic measurements

Magnetisation (M) with respect to the applied magnetic field (H) (left) and magnetisation with respect to decreasing temperature (right). Reprinted with permission from Faraz *et al.* (111).

Figure 8: Magnetolectric domain switching

Piezoelectric response of B6TFMO to applied magnetic field cycle (H). Redrawn with permission from Faraz *et al.* (111).

How then can researchers confidently claim that a candidate multiferroic material is free from interfering secondary phases? The approach developed by the Schmidt *et al.* (82) involved applying statistical methodology to analyse microstructural results. While this approach must necessarily make assumptions about the type of impurities and their potential distribution throughout a material, it is a powerful tool that can be utilised to determine the possible contribution towards magnetisation that may be attributed to undetected magnetic impurities. This statistical approach, discussed further in Section VII.1, enabled conclusion, with $\geq 99.95\%$ confidence, that the ferromagnetic signature in $\text{Bi}_6\text{Ti}_{2.99}\text{Fe}_{1.46}\text{Mn}_{0.55}\text{O}_{18}$ is attributed to the Aurivillius phase and that a single phase room temperature multiferroic material was developed (111).

VII.2. Statistical analysis

A method of statistical inference was initially developed involving the refutation of the Null Hypothesis. The Null Hypothesis proposes that there is no statistically significant difference between specific populations. To give an example in terms of STEM-EDX measurements, applying the Null hypothesis would imply that the measured area, 10 nm^2 for example, is representative of the entire sample. The method developed here can quantify with a specific confidence level what probability a measured volume is representative of the entire sample. A full statistical analysis is required in order to assign a confidence level of the phase purity of the material. This requires a series of measurements at varying sample volumes and instrument resolutions. The method is outlined next and full details are to be found in the paper by Schmidt *et al.* (82).

VII.1.1 Statistical inference of a single measurement

With a single measurement approach, it is assumed that secondary phases present in the sample are evenly distributed throughout the sample and do not interact with each other. Their distribution in the sample can then be represented by the Poisson distribution, which gives the probability that N impurities will be found in a known volume (density, ρ) [1]

$$P(N, \rho) = \frac{(\rho V)^N}{N!} e^{-\rho V} \quad [1]$$

The probability of finding no impurities ($N=0$) in a known volume (V) is then given by,

$$P(0, \rho) = e^{-\rho V}$$

Fixing the desired confidence level, $\gamma = 99.5\%$ for the case of this example gives,

$$\sum_{m=0}^N P(m, \rho_u^N) = 1 - \gamma \quad [2]$$

It follows that for any impurity density ρ larger than ρ_u^N the probability of finding N impurities in volume (V) is below $1 - \gamma = 0.5\%$. If no impurities are observed then equation [2] can be solved as follows,

$$\rho_u^0 \frac{-\ln(1-\gamma)}{V} \approx \frac{5.3}{V}$$

Therefore, if N or fewer impurities are found in a scan of volume (V) then, with a confidence of 99.5%, it can be concluded that,

$$\rho < \rho_u^N \quad [3]$$

This establishes an upper bound for unknown impurity density ρ .

VII.1.2 Grain size distribution

The previous example assumes only one type of impurity is present in a sample. We now take a representative example, such as Fe_3O_4 , as a potential magnetic impurity and assume for simplicity that the impurities are spherical. The grain size distribution can then be given as $p_G(d)$ where for small Δd , $p_G(d)\Delta d$ represents the density of impurities with diameter from d to $d+\Delta d$. Generalising equation [3] for the upper bound the size dependent distribution in volume (V), of impurities N , with a minimum detectable size d_m , it can be concluded with 99.5% confidence is given by,

$$\int_{d_m}^{\infty} dq p_G(q) < \rho_u^N$$

VII.1.3 Series of measurements

The preceding functions correspond to only one volume scan. In reality, analysis will involve a number of scans (K), would be performed at a variety of scan volume sizes (V_K) and have varying minimum detection sizes d_k . In this case, index $k = 1, \dots, K$ represents individual scans starting at large d_k ($d_k > d_{k+1}$) that have N_k or fewer impurities. Imposing an upper physical bound on grain size of $d_0 > d_{k+1}$, the density of

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impurities (ρ_k) larger than the minimum size d_k in the grain size distribution $p_G(d)$ is given by,

$$\rho_k = \int_{d_k}^{d_0} p_G(q) dq$$

For one scan k , the probability of finding N_k or fewer impurities is,

$$P_k(N_k) = \sum_{m=0}^{N_k} P(m, \rho_k)$$

For the sequence of scans $k = 1, \dots, K$, the probability of finding N_k or fewer impurities is,

$$P = P_1(N_1) P_2(N_2) \dots P_k(N_k)$$

Assuming that no impurities larger than the minimum detectable size for the analysis technique used are observed in the series of scans, then the probability of a zero outcome is,

$$P(0) = P_1(0) P_2(0) \dots P_k(0)$$

Assuming the impurities are spherical, then the volume fraction φ_k of impurities between sizes d_k and d_{k-1} in the grain size distribution $p_G(d)$ is,

$$\varphi_k = \int_{d_k}^{d_{k-1}} dq p_G(q) \frac{4}{3} \pi \left(\frac{q}{2} \right)^3 \leq \left[\int_{d_k}^{d_{k-1}} dq p_G(q) \right] \frac{\pi}{6} d_{k-1}^3$$

Then assuming a worst case scenario, with a 99.5% confidence level, the upper limit $\varphi_{k,u}$ of impurity volume fraction φ_k and grain size d_k to d_{k-1} is given by,

$$\varphi_k < \varphi_{k,u} = \frac{-d_{k-1}^3}{\sum_{j=k}^k V_j} \frac{\pi}{6} \ln(1-\gamma) \approx 2.8 \frac{d_{k-1}^3}{\sum_{j=k}^k V_j} \quad [4]$$

VII.1.4 Effect of impurity inclusions on remanent magnetisation

The upper bound of the volume fraction of a secondary impurity phase has now been established. As this statistical methodology is applied to the analysis of potential magnetic materials, quantifying the contribution from secondary magnetic impurity phases would be extremely valuable. The maximum contribution to remanent magnetisation from impurities of sizes d_k to d_{k-1} , can be given as

$$M_{r,k,u} = \phi_{k,u} M_{r,F}(d_{k-1}) \quad [5]$$

Continuing the example with Fe_3O_4 as impurity, then $M_{r,F}(d)$ is the remanent magnetisation from the Fe_3O_4 grains with diameter d . Assigning values to the example, $M_{r,F}(d) = 0$ at grain sizes $< 5\text{nm}$ and values of $M_{r,F}(d) = 10 \text{ emu/g}$ for $5 \text{ nm} < d < 20 \text{ nm}$ and $M_{r,F}(d) = 20 \text{ emu/g}$ for grain sizes $> 20 \text{ nm}$. The upper bound on the contribution for impurity Fe_3O_4 to the remanent polarisation is,

$$M_{r,u} = \max_{W_1, \dots, W_K} \left\{ \sum_{k=1}^K W_k M_{r,k,u} \right\}$$

The parameter $W_1, \dots, W_K$ must fulfil the constraint,

$$\sum_{k=1}^K W_k = 1$$

Finally, it can be concluded with a confidence level $\gamma = 99.5\%$ that the upper bound of the contribution from the magnetic impurity phase M_r is given by,

$$M_{r,u} = \max_{W_1, \dots, W_K} \{ M_{r,k,u} \}$$

VIII. Cation partitioning within Aurivillius structures

The ability to vary composition and the number of perovskite layers (m), yields different numbers of symmetrically-distinct B -site locations within the Aurivillius framework. The question of how cations distribute over the available B -sites is of particular importance since it undoubtedly affects the attempted properties.

A necessary condition for magnetic order is the coexistence of structural ordering of magnetic cations among selected crystallographic sites. Density functional theory calculations of $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ ($m=4$) predicts rather strong couplings of the order of $J_{\text{NN}} \sim 40\text{--}50$ meV for Fe^{3+} cations in nearest neighbour (NN) positions (36). Conversely, for Fe^{3+} cations distributed in next-nearest-neighbour (NNN) positions, the coupling is relatively weak ($J_{\text{NNN}} \sim 1\text{--}2$ meV) and becomes negligible among second-nearest neighbours. An increase in NN interactions would lead to an increase in long-range magnetic order, thereby yielding increased magnetisation values. We also know from the work of Goodenough and co-workers that the juxtaposition and arrangement of Mn-O-Fe and Mn-O-Mn linkages is important in determining the existence of ferromagnetism, or anti-ferromagnetism, depending on the valence states of the ions concerned and the bond lengths (112, 113). Preferential partitioning of magnetic cations provides means for increased magnetic percolation and stronger effective magnetic coupling compared to a structure with an even or random distribution of magnetic cations over the available perovskite layers. Therefore, determining the *B*-site distribution of the magnetic cations in the Aurivillius phases is critical for understanding the observed magnetic properties.

Prior to 2015, our knowledge of magnetic cation partitioning in the Aurivillius phases (23, 33, 114-116) had mainly depended on deductions from structural refinement and statistical methods. Previous observations of magnetic cation partitioning within the Aurivillius perovskite layers were determined by Rietveld refinement of X-ray and neutron powder diffraction data. In the $m=3$ compound $\text{Bi}_2\text{Sr}_2\text{Nb}_2\text{MnO}_{12-\delta}$, Mn ions were reported to order into the central layer, away from the $[\text{Bi}_2\text{O}_2]^{2+}$ layers. Giddings *et al.* (116) inferred from Rietveld analysis of neutron diffraction data of $\text{Bi}_5\text{Ti}_3\text{CrO}_{15}$ ($m=4$), that Cr ions partition partially into the central two layers. Lomanova *et al.* (23) used Mössbauer spectroscopy to study the $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ system where $3.5 \leq m \leq 9$. They describe that for $m < 7$, there is a preference for Fe cations to partition away from the perovskite blocks adjacent to the $[\text{Bi}_2\text{O}_2]^{2+}$ layers, but that for $m \geq 7$, Fe and Ti cations are randomly distributed over the available perovskite *B*-sites. This is consistent with DFT calculations where a slight preference for Fe ions to partition into the inner sites of the 4-layered $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ is predicted (36). Conversely, Hervoches *et al.* (33) were unable to detect any departure from a random distribution of Fe ions in the $m=4$ structure $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$, either by Rietveld refinement of neutron diffraction data, or by Mössbauer spectroscopy. By contrast, as observed by Rietveld refinement of X-ray diffraction data, the $m=5$ $\text{Bi}_6\text{Ti}_3\text{Fe}_2\text{O}_{18}$ structure exhibits partial-partitioning of the Fe cations away from the perovskite blocks adjacent to the $[\text{Bi}_2\text{O}_2]^{2+}$ layers, and into the central three perovskite layers (117). Statistical analysis of extended X-ray absorption fine structure (EXAFS) data for this $m=5$ compound has also indicated a preference for the Fe cations to occupy the 'inner' sites within the perovskite layers (115). However, EXAFS is a statistical technique whereby experimental information on unique

octahedral sites is refined to theoretically calculated structural models, and no information can be derived on the exact location of these cations, or the extent of cation partitioning.

More recently, atomic-resolution scanning transmission electron microscopy (STEM) techniques by Campanini *et al.* (9) provide direct observations of Fe cation locations in thin films of $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ ($m=4$) prepared by pulsed laser deposition on lattice matched substrates. Due to the relaxed state of these samples, it was found that the distribution of Fe cations gives rise to preferential mixed configurations, where the Fe cations occupy one inner and one outer octahedral *B*-site of the four perovskite blocks. Direct evidence of Fe cation partitioning in the $m=9$ $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ system was presented by Huang *et al.* (118) by means of HAADF-EELS (high-angle annular dark-field electron energy loss spectroscopy) analysis. In this work, Fe^{3+} was observed to partition away from the central layers of the perovskite blocks and towards the $[\text{Bi}_2\text{O}_2]^{2+}$ layers. This is an interesting result which differs with the earlier work (23) that implied a tendency for Fe cations to partition into the central perovskite blocks layers or, for compositions with $m \geq 7$, to be randomly distributed. We comment that the disparity between different authors' observations of Fe cation partitioning in different $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ systems may be a consequence of differences between sample preparation methodologies.

Although Huang *et al.* (118) do not remark upon this disparity between their observations and the other reported works in $\text{Bi}_{10}\text{Fe}_6\text{Ti}_3\text{O}_{30}$ ($m=9$). They make the valuable observation that the structural partitioning of magnetic cations may be connected to the magnetic behaviour of this type of material. This is similarly important for the Mn-containing $\text{Bi}_6\text{Ti}_x\text{Fe}_y\text{Mn}_z\text{O}_{18}$ (B6TFMO; $x = 2.80$ to 3.04 ; $Y = 1.32$ to 1.52 ; $Z = 0.54$ to 0.64) system (3, 111), for understanding the origin of the unexpected room temperature ferromagnetism, and for explaining why it is that manganese-containing samples in particular demonstrate multiferroic behaviour.

Direct atomic-scale visualisation of magnetic cation partitioning in the B6TFMO system was demonstrated by Keeney *et al.* (119) using atomic-resolution aberration-corrected HAADF-STEM combined with EDX (energy dispersive X-ray analysis) and EELS (Fig. 9) for two different chemical vapour deposited thin film samples. For both samples, there is a notably increased ($\sim 20\%$) EDX signal for Ti at the outer perovskite layers compared with the intermediate and centre perovskite layers. Overall, there appears to be a slight preference (3 to 5% increase) for Fe cations to partition into the inner perovskite sites compared with the outer sites. This only slight preference for Fe to partition into the inner sites is consistent with Mössbauer data (23) and DFT calculations for the 4-layered $\text{Bi}_5\text{Ti}_3\text{FeO}_{15}$ (36). On the other hand, a striking decrease in Mn signal is observed at the outer perovskite layers, an obvious drive for Mn to partition into the intermediate layers and a clear preference (17 to 20%) for partitioning

to the central layer. This results in a notable increase in *B*-site magnetic cation composition at the inner sites, from ~47% when considering a disordered structure, to >54% with magnetic partitioning. This partitioning of magnetic cations into the central perovskite layers increases the probability of the potentially-ferromagnetic Fe-Mn and Mn-Mn NN interactions, which is nearly a 90% increase within the central layer. The capability to directly observe cation type and location via these experiments is pivotal in explaining pathways to long-range magnetic order and the distinct room temperature multiferroic properties of the B6TFMO material system.

In order to optimise ferromagnetic response in established multiferroic materials or to design new layered-structured multiferroics, it is useful to understand what factors drive cation partitioning. Garcia-Guaderrama *et al.* (117) use Kikuchi's model (116, 120) for Aurivillius phase materials. In this model, which continues from Armstrong and Newnham (20), the “natural” *a*-spacing (*a_B*) of the [Bi₂O₂]²⁺ layer is determined as 3.78 Å, whereas the “natural” *a_p*-spacing of the perovskite blocks in bismuth titanate (Bi₄Ti₃O₁₂) is 3.88 Å. The actual value of *a* for Bi₄Ti₃O₁₂ is 3.83 Å; roughly halfway between the [Bi₂O₂]²⁺ layer and perovskite block values.

Figure 9: Atomic resolution chemical mapping images

Representative atomic resolution chemical mapping images for B6TFMO. (a) annular dark-field image and (b) to (f) corresponding EDX chemical composition maps: (b) overlay map showing annular dark-field image (white), Bi (green), Ti (blue), Mn (pink), Fe (red), (c) Bi map, (d) Ti map, (e) Mn map, (f) Fe map. (g) EELS chemical composition maps of a different region of B6TFMO with Ti in green and Mn in blue. Taken from Keeney *et al.* (119). under the terms of the Creative Commons CC BY licence which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This places the perovskite blocks under compression, and the $[\text{Bi}_2\text{O}_2]^{2+}$ layers under tension and generates a strain energy that will drive cations larger cations away from the layers closest to the $[\text{Bi}_2\text{O}_2]^{2+}$ layers. Giddings *et al.* (116) put forward two reasons for the partitioning of Cr^{3+} away from the outer layers for $m=4$ $\text{Bi}_5\text{Ti}_3\text{CrO}_{15}$. The first reason is the preference of Ti^{4+} to occupy more-distorted octahedra because of its d^0 electron configuration, which exhibits a strong tendency for off-center displacement due to the second-order Jahn-Teller effect. This reason was also proposed by Lomanova *et al.* (23) during analysis of several different $\text{Bi}_{m+1}\text{Fe}_{m-3}\text{Ti}_3\text{O}_{3m+3}$ ceramics. The Shannon site distortion parameter (121) Δ_n was used to determine the degree of octahedral distortion for the two type of octahedra in the $m=4$ system. They determined that Δ_6 is 5.2 and 5.6 for the outer and inner octahedral respectively at 295K. This would not drive cation partitioning at 295K, but at 970K (much closer to the compound synthesis temperature) the numbers are 6.17 and 0.75 respectively, providing a clear driving mechanism. Giddings *et al.* (116) also provide a second possible mechanism based upon a preference for the more-highly-charged Ti^{4+} cation to favour locating to the outer sites in order to be closer to charged $[\text{Bi}_2\text{O}_2]^{2+}$ layers, thereby maximising electrostatic interactions. They support this with Madelung energy calculations which indicate an energetic preference for the partitioning. Therefore, the three potential mechanisms to drive magnetic cation partitioning are: the strain-energy considerations of Kikuchi (120), the preference of Ti^{4+} to occupy more-highly-distorted octahedra and electrostatic energy considerations.

The chemical vapour deposition technique used to synthesise the B6TFMO samples (111) does not enforce any layer-by-layer ordering of the precursors during the deposition process, therefore cation partitioning must occur as a natural part of the growth process. Δ_n values for B6TFMO were calculated to be 0.70, 0.46 and 0.05 for the outer, intermediate and central layer octahedral, respectively. These are much smaller than the values reported for $\text{Bi}_5\text{Ti}_3\text{CrO}_{15}$, and would be further reduced at the synthesis temperature (1100K) (116). Therefore it was concluded (119) that site asymmetry is not a strong drive for cation partitioning in the B6TFMO system. When considering that a substantial part of the Mn in the B6TFMO system will be present as Mn^{2+} during the 1100K synthetic process and that Mn^{2+} is 33% bigger than Ti^{4+} , but Fe^{3+} is only 6% bigger than Ti^{4+} , there is a much larger strain-energy incentive towards partitioning of Mn^{2+} away from the $[\text{Bi}_2\text{O}_2]^{2+}$ layers than Fe^{3+} . Likewise, we would expect that the divalent Mn^{2+} would have a stronger preference than trivalent Fe^{3+} for partitioning away from the outer oxygens of the $[\text{Bi}_2\text{O}_2]^{2+}$ layers. On the other hand, Fe^{3+} would still, as a trivalent ion slightly bigger than Ti^{4+} , have some drive for partitioning. Therefore Kikuchi strain energy (120) and electrostatic interactions are the most likely mechanisms for explaining the observation of a >17% increase in the B-site proportion of Mn at the inner layers, compared with only a 3-5% increase in Fe partitioning. Interestingly, Birenbaum *et al.* (5, 122) propose that further control of

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multiferroic properties can be achieved with the introduction of external epitaxial strain, which can further tailor the extent of magnetic cation partitioning and can allow tuning of ferroelectric polarisation.

Crystallographic defects, such as out-of-phase boundary (OPB) and stacking fault defects are a common occurrence in materials of high structural anisotropy, such as the Aurivillius phases (4, 119, 123, 124). OPBs are boundary defects characterised by displacement by a fraction of a lattice parameter (c/x) between two neighbouring regions parallel to the z -direction. When present at high enough densities, OPBs can generate peak splitting in X-ray diffraction patterns, due to out-of-phase alignment of domains within a diffracting volume (4).

Figure 10: HAADF-STEM images

Representative atomic resolution images of B6TFMO in a region of the crystallite displaying OPBs / stacking faults. HAADF-STEM images of (a) lower magnification and (b) higher magnification. The numbers displayed in red designate the number of perovskite layers (m) in the region designated by the red bar. The majority of the sample has an $m=5$ structure. Yellow arrows demonstrate the position of the OPBs and blue rectangles indicate stacking fault regions. Taken from Keeney *et al.* (119) under the terms of the Creative Commons CC BY licence which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Advances in electron microscopy, e.g. optimised HAADF-STEM, allow us to splendidly view the atomic structure of OPBs at the local scale. These appear as ‘steps’ as viewed edge-on in Fig.10 (119). OPBs can form when the *c*-axis is inclined with respect to the substrate surface, allowing propagation of OPBs through the film (denoted by the arrows in Fig.10 (a)) or when adjacent, out-of- phase nuclei meet during growth (designated by arrows A/B/C in Fig.10 (b)).

Figure 11: HAADF-STEM dark-field and EDX images

Representative atomic resolution images for B6TFMO in a region of the sample displaying OPBs / stacking faults. (a) and (c) annular dark-field images and (b) and (d) corresponding EDX chemical composition overlay maps showing annular dark-field image (white), Bi (green), Ti (blue), Mn (pink), Fe (red). Yellow arrows demonstrate the positions of the OPBs, the blue rectangle A signifies a stacking fault region and the green ellipsoid B designates a region in the vicinity of an OPB. The numbers displayed in red designate the number of PK layers (*m*) in the region designated by the red bar. The majority of the sample has an *m*=5 structure. Taken from Keeney *et al.* (119) under the terms of the Creative Commons CC BY licence which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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These can be accompanied by an insertion of an 'extra' perovskite block, giving small regions having different m -layers, as evident by $m=6$ regions in both Fig.10 (a) and (b). The Aurivillius phases are also susceptible to atomic stacking faults. These are sub-unit-cell intergrowths of different m -layers (e.g. $m=6$, $m=4$) of the homologous series and are associated with an overall change in chemistry at the defect region. Examples of typical stacking faults are highlighted by the blue rectangles in Fig.10 (b). Stacking faults can also terminate in an OPB. The type and density of these defects can vary widely from sample to sample and from grain to grain within samples (119). A comprehensive review of the morphology, structure, and nucleation mechanisms of OPBs in epitaxial films of layered complex oxides is presented by Zurbuchen *et al.* (4).

Compositional analysis of the defect regions would be very valuable in understanding what effects the physical disruptions of the lattice have on the defect chemistry. The average compositional distribution across the layers could (at least in theory) be obtained from accurate neutron diffraction, or perhaps even XRD using synchrotron techniques, but these techniques cannot yield localised defect information. The most efficient method to detect changes in chemistry at the defect is by atomic resolution mapping. In these HAADF images, we can clearly see that physical interruption of the lattice is compensated by a deficiency or excess of bismuth atoms. This is further demonstrated by atomic-resolution EDX (Fig.11). Atomic resolution chemical mapping of a stacking fault region in B6TFMO (blue rectangle A in Fig.11 (a)) reveals that the percentage of Ti is increased (~12%) and the percentage of Mn is drastically decreased (~13%) locally at the defect. The considerable effect that an OPB has on the local stoichiometry in the vicinity of the OPB is demonstrated by the green ellipsoid B in Fig.11 (a). A substantial increase (~30%) in Ti compensates for the deficiency in Bi, while the Fe concentration is depleted (~17%) and there is virtually no Mn present at the OPB defect region. It is important to note that while the overall effect of the defect on the total proportions of Ti, Fe and Mn across the average unit-cell is not significant, there is a significant ~13% (~8% Mn and ~5% Fe) increase in magnetic cation partitioning to the inner perovskite layers (layers 3/4/9 of Fig.11 (c)) for regions between OPBs, compared with a ~9% (~6% Mn and ~3% Fe) increase in partitioning to the inner perovskite layers for defect-free regions. It therefore appears that disruptions of the Aurivillius phase lattice by OPB defects result in further partitioning of magnetic cations to the inner perovskite layers of B6TFMO. Thus, changes in local chemistry at the defects and corresponding changes to magnetic cation distribution in the defect regions could be significant in determining magnetic behaviour in B6TFMO and future work to control defect levels could be key for optimised and reproducible multiferroic properties.

IX. Conclusion

The Aurivillius phase materials are very flexible frameworks for a wide variety of applications, including opto-electronic, sensing, actuator, memory storage and more recently they show potential towards recyclable photocatalysts (125). As well-established ferroelectrics, Aurivillius phase materials, e.g. $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ($m = 2$) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ($m = 3$) have been developed for commercial use in Fe-RAM (ferroelectric random access memory) devices (7, 126, 127).

More generally, devices based on out-of-plane ferroelectric tunnel junctions (FTJs) (128) and composite magnetoelectric tunnel junctions (129-131) using a variety of materials are currently being developed for use in neuromorphic computing architectures. A challenge to commercialisation is the formation of polarisation induced surface charges induced by the out-of-plane polarisation which can produce a depolarisation field of magnitude inversely proportional to the dimensions of the ferroelectric. This means that below a critical thickness, out-of-plane ferroelectricity will be suppressed, leading to a lack of stability and reproducibility in vertical tunnel junctions at reduced dimensions. As discussed in this review, while Aurivillius phase thin films demonstrate out-of-plane ferroelectric polarisation, crystal symmetry dictates the major polar axis of B6TFMO is along the in-plane direction, therefore they demonstrate much greater in-plane (up to 50 mC/cm^2) than out-of-plane (approx. 4 mC/cm^2) ferroelectric polarisation and piezoresponses.

Recently, devices have been proposed based on an in-plane tunnel junction (132-135), which would not be hindered by competing depolarisation fields upon scaling down to ultra-thin dimensions, meaning that higher ON:OFF tunnelling current ratios can be achieved with non-destructive read operations. So far, no such in-plane devices exist in practice, only device concepts based on theoretical simulations of monochalcogenides have been proposed. Given the established in-plane ferroelectricity at Curie temperatures above 650°C and the fact that they can be synthesised by several scalable growth methods (3, 9, 111, 124), the Aurivillius phases are perfect candidates for utilisation in novel in-plane devices enabling ferroelectric control of tunnelling electron resistance. However, materials optimisation is required to produce ultra-thin (10 nm) films and advanced lithography techniques are necessary to achieve devices having tunnelling widths of 10 nm.

As described in this review, the Aurivillius phases are a particularly attractive class of oxides for the design of single phase multiferroic systems as they can accommodate substantial amounts of magnetic cations within a strongly ferroelectric system. Multiferroics combine ferroelectric and ferromagnetic properties, allowing for novel ways of manipulating data and storing information. They have been identified by companies such as Intel (78, 79) as leading contenders for enabling beyond CMOS data storage, whereby coupling between the ferroelectric and ferromagnetic states permits energy-efficient switching of memory states and enhanced logic densities. Not only could multiferroics find application in high storage density, low-power memory devices that can be electrically written and magnetically read, the unique commercial potential lies in the opportunity for the creation of a multi-state memory storage device based on electroresistance/magnetoresistance differences created when electrons tunnel through an ultra-thin multiferroic thin film/junction. This would significantly advance data storage capabilities and sustain consumer demand for increasing levels of data creation. As miniaturisation of electronic devices continues, a crucial requirement for materials in data storage applications is the enhancement of their functional properties at the nano-scale. This is supported by a recent review on magnetoelectric multiferroics (76), which emphasises that a critical requirement for future technologies is the demonstration of room temperature magnetoelectric coupling at the 10 nm length scale. This is recognised within the community as a challenging task due to the lack of optimised room temperature multiferroic materials. Room temperature multiferroic Aurivillius phases, such as $\text{Bi}_6\text{Ti}_x\text{Fe}_y\text{Mn}_z\text{O}_{18}$ (3, 82, 111, 119) are well-positioned to meet those challenges. However reproducible and enhanced ferromagnetic responses are required. It would therefore be useful to direct the next chapter of development towards epitaxial growth of sub-10 nm films where film orientation, strain, magnetic cation partitioning and defects can be controlled, thereby enabling enhancement of multiferroic properties for use in technologically relevant devices.

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Complementary information on authors:

Jennifer Halpin obtained a BSc. Chemistry from University College Cork, Ireland in 2015. Beginning work at Tyndall National Institute, Cork, in 2015 she obtained a MSc. Chemistry for work on the development of photoanode materials for solar water splitting applications in 2016 and is currently a PhD candidate focusing on the synthesis and characterisation of Aurivillius Phase Materials at Tyndall National Institute, Cork.

Dr. Lynette Keeney received a B.Sc. in chemistry in 2001 from National University of Ireland (NUI), Galway and a Ph.D. in inorganic chemistry in 2004 also from NUI, Galway where she won five University awards for her undergraduate and postgraduate studies. Before joining Tyndall-UCC in 2008, she worked as a Research Scientist in Charles River Laboratories, Pre-clinical Services, Montreal Inc. in method development and validation of analytical research studies. Dr. Keeney has a strong background in the synthesis of complicated metal oxide thin film systems by chemical solution deposition and chemical vapour deposition methods and characterization of these systems for potential data storage applications. Her research interests are the investigation of ferroelectric, ferromagnetic and multiferroic materials and was one of the Irish representatives for the COST (European Cooperation in Science and Technology) Action MP0904 (Single and multiphase ferroics and multiferroics with restricted geometries (SIMUFER)). Dr. Keeney is a member of the International Advisory Board of ECAPD (European Conference on Applications of Polar Dielectrics), the Royal Society of Chemistry (MRSC), member of the IEEE Ultrasonics, Ferroelectrics and Frequency Control Society and is Tyndall-UCC representative on the Microscopy Society of Ireland Council. In 2015, Dr. Keeney was awarded a prestigious Royal Society/Science Foundation Ireland University Research Fellowship for her research project: 'Memories are made of this: Multiferroics Research for Future Generation Memories'. Dr. Keeney received the UCC Early Stage Researcher of the Year Award in 2015.

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