Chapter 9

Multiferroicity in Aurivillius Based $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Ceramics: An Overview, Future Prospective and Comparison with Ferrites

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Abstract

The growing modern society demands more new generation devices to fulfil their requirements. This has forced the scientific community to develop multifunctional smart devices. Aurivillius based $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics are one of the leading families of oxide materials, which attract immense attention due to their electrical, ferroelectric, optical, and dielectric properties. These materials have gained special attention due to their numerous device applications such as magnetic recording, sensors, read head technology, spintronic devices, switching devices, data storage devices and multiple state memory devices etc. Multiferroic are the materials in which two or more than two ferroic orders exist simultaneously. This chapter focuses on the possibility of existence of multiferroic behaviour in Aurivillius based compounds specially $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Firstly, we have discussed the basics of multiferroics and their types and the magnetoelectric effect. The effect of different dopants in originating the multiferroism in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ have been reviewed and discuss in detail. At the end comparison of multiferroic and ferrite materials and their future perspective have been discussed.

Keywords

Multiferroics, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Ferroelectrics, Ferromagnetic

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1. Introduction

Functional electronics and magnetic materials are playing a significant role in modern technology. Ferroelectric materials are used in computers for manufacturing of ferroelectric random-access memory (Fe-RAM), whereas, magnetic materials are generally used for recording and data storage. Current technology is following a trend towards device miniaturization. This trendy behaviour has led to the growing interest in combining the ferroelectric and magnetic properties in multifunctional devices.

Multiferroics are materials in which two or more primary ferroic orders exists simultaneously [1-2]. The term ‘multiferroic’ was introduced by Schmid in 1994 to

define materials in which two or more than two types of ferroic order occurs simultaneously in the same phase as shown in Figure 1.

One of the most appealing aspects of multiferroics is called magnetoelectric coupling. There are very small group of materials that can show both magnetic and electric orders simultaneously [3].

In these materials, the magnetic field can not only control magnetization but also give rise to ferroelectricity, or electric field can reorient polarization as well as spin arrangements. This property offers an extra degree of freedom and provides the possibility to create new devices based on these materials.

The existence of multiferroicity is determined by number of factors, including crystal structure, symmetry, electronic properties, and chemical properties. There are only thirteen-point groups that can gives rise to multiferroic behaviour [3-4]. The origins of ferromagnetism and ferroelectricity are different. Ferromagnetism needs transition metals with unpaired $3d$ electrons and unfilled $3d$ orbitals; while ferroelectric polarization needs transition metals with filled $3d$ orbitals. Due to different origins, the single phase multiferroic compounds are few in number especially magnetoelectric multiferroics [5-6].

Figure 1: Relationship between ferroelectric, ferromagnetic, multiferroic and magnetoelectric materials [1].

2. Types of multiferroic materials

Multiferroic materials are classified into two types:

- i. Single phase multiferroics
- ii. Composite multiferroics

Single Phase Multiferroics: Single phase multiferroics are those materials that show both ferroelectric and ferromagnetic order [7-11]. Recently, various multiferroic materials have been discovered in which a polar state is induced by different types of ordering, these materials are also known as “improper ferroelectrics”. Khomskii classified single-phase multiferroics into two groups and other subgroups, according to the physical mechanism behind ferroelectricity [12]. The grouping of single-phase multiferroics is as given below:

Figure2: Grouping of single phase multi-ferroic materials.

Type-I multiferroics are those materials in which ferroelectricity and magnetism have different sources; usually they show large polarization values and ferroelectricity appears at much higher temperatures than magnetism. This difference in transition temperatures reveals that both orders involve different energy scales and mechanism, which provokes to occurrence of weak magnetoelectric coupling. In this class of multiferroic materials multiferroicity is not due to ferroelectricity, because the magnetic and ferroelectric order have two different sources. In this kind of materials, the origin of ferroelectricity is from different sources such as:

- i. Ferroelectricity due to lone pair
- ii. Ferroelectricity due to charge ordering
- iii. Geometric Ferroelectricity

On the other hand, type-II multiferroics corresponds to the material, in which magnetism causes ferroelectricity, due to which there is a strong coupling between the two orders. These materials show smaller electric polarization values and ferro-electricity always appears at lower temperature than magnetic order. These materials are in turns separated into two subgroups.

- i. Ferroelectricity induced by spiral magnets
- ii. Ferroelectricity induced by collinear magnets

3. Magnetoelectric effect

Multiferroic materials exhibit very interesting features; they show ferroelectric properties as well as magnetic properties, which points to multifunctional applications. Moreover, multiferroic likely to exhibit the magnetoelectric effect (ME), which is the phenomenon of tuning of magnetic properties with the application of an external electric field and electric properties with magnetic field. In other words, we can control magnetic properties by electric field and electric properties by magnetic field [13-15]. The ME effect provides an additional degree of freedom for devices fabrication such as multiple state memories in which data can be written magnetically and read electrically and vice versa [16]. The ME effect can be linear or / and non-linear with respect to external fields. This effect was first observed by Rontgen in 1888 and Pierre Curie in 1894 in two independent studies. Rontgen found that, when a dielectric material is moved in an electric field, it become magnetized [17, 18]. In 1894, the possibility of intrinsic coupling between magnetic and electric properties was introduced by Curie on the basis of magnetic symmetry [5]. Dzyaloshinskii predicted this effect in the single phase antiferromagnet Cr_2O_3 based on the symmetry consideration and Astrov confirmed this prediction experimentally in 1960 [19-21]. This was a breakthrough in magnetoelectric effect and afterward, the research was carried on various materials. Till now, many materials that exhibit the magnetoelectric effect has been discovered and synthesized.

Restraining our discussion to oxide materials, especially perovskite compounds, it was proven that ferroelectricity and magnetism have different origins. The ferroelectricity originates from the B-site d^0 electrons. Whereas, the magnetic properties require d^k electrons ($k \neq 0$). Moreover, the existence of polarization requires distorted asymmetric crystal structure, whereas ferromagnetism requires a symmetric structure. This concept has been proven experimentally on multiferroics.

In case of perovskite materials, it is realized that these materials do not have the same mechanism of ferroelectricity. For example, in BaTiO_3 , the central Ti ions play the key role, whereas in PbTiO_3 , the lone-pair Pb ion play the leading role [22-24]. On the other hand, in BiFeO_3 ferroelectricity is mostly dominated by the $6s^2$ lone-pair of Bi ions. Thus, the polarization in BiFeO_3 comes from the A-site (Bi^{3+}) ions, while magnetization comes from B-site (Fe^{3+}) ions. The same concept has been applied in designing and fabrication of new class of oxide materials.

4. Aurivillius Based Layer-Structured Ferroelectrics

The most promising ferroelectric material for Random access memories (RAMs) has been considered as Lead zirconium titanate (PZT). But PZT has some problematic issues such as fatigue, non-eco-friendly nature of lead, high operating voltage and low Curie temperature [25]. In comparison with non-layered perovskite ferroelectrics such as PZT and strontium bismuth tantalate (SBT), the bismuth layer-structured ferroelectrics are the promising candidates. These materials have several advantages such as fatigue-free, lead free, low operating voltage and high curie temperature. This makes the study and understanding of these materials interesting, and hence there is hunt for new materials with improved properties.

Bengt Aurivillius has discovered the family of layered structured materials, in which layers of bismuth oxide are sandwiched between perovskite structure layers [26-28]. The unit cell of Aurivillius compounds may be described as an assembling of bismuth oxide layers $(\text{Bi}_2\text{O}_2)^{2+}$ interwoven with pseudo-perovskite layers $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$. The general formula for the compound is $(\text{Bi}_2\text{O}_2)^{2+} (\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where m is the number of perovskite unit sandwiched between bismuth oxide layers, and A is a mono, di or trivalent cation, and B is a tri, tetra, penta or hexavalent cation. In the $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ unit cell, B-site ions are enclosed by oxygen octahedral and A-site ions occupy spaces in the framework of BO_6 octahedral.

In the family of layered structured materials, the best-known compound is $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can be represented by the general formula $(\text{Bi}_2\text{O}_2) [(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})]$ with $m = 3$, consists of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets alternating with $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ perovskite like layers [27] as shown in Figure 3.

Figure 3: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Crystal Structure [27].

In Figure 3, the Ti ions are enclosed by oxygen octahedral, whereas, Bi-ions occupy the spaces in the framework of TiO_6 octahedral. Along the c-axis, the Perovskite units $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ are enclosed with $(\text{Bi}_2\text{O}_2)^{2+}$ layers. Subbarao has first discovered ferroelectricity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [29]. The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has attracted great interest due to its applications in optical devices and ferroelectric memories [25]. The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ exhibit orthorhombic crystal structure and has Curie temperature (T_c) around 675 °C [30-32].

5. Origin of multiferroicity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

Multiferroic materials are of great technological importance, since ferroelectricity and ferromagnetism co-exist in same phase at room temperature. Due to the existence of coupling between the two orders, it will be possible to write the data bit with an electric field and read it with a magnetic field and vice-versa. Various research groups are working on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, to bring the two ferroic orders in single phase material along with coupling between them at room temperature.

In the field of ferroelectric oxides, study of the Aurivillius family multiferroic materials is a challenging area for diverse applications. The first report on the possibility of

multiferroic properties was published by Lu *et al.* [33], who have investigated that partly substituting Ti ions with Fe ions leads to weak ferromagnetism at room temperature. In the year 2010 Chen *et al.* [34] reported the room temperature magnetoelectric coupling in $\text{Bi}_4(\text{Ti}_1\text{Fe}_2)\text{O}_{12-\delta}$ ceramics. They use conventional solid state reaction method to synthesize the compound. In the same year Chen *et al.* [35] has again reported the enhancement in multiferroic properties $\text{Bi}_4(\text{Ti}_1\text{Fe}_2)\text{O}_{12-\delta}$ ($x = 0, 1, 1.5, 2$) ceramics. They reported maximum remnant polarization ($2P_r = 4.1 \mu\text{C}/\text{cm}^2$) and maximum remnant magnetization ($M_r = 3 \times 10^{-3} \text{emu/g}$). Due to high losses and conduction, the materials exhibit high losses and results in poor ferroelectric properties.

It has been reported that ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ have been improved by substitutions at either A-site or at the B-site or at the combination of both sites. It was reported by Park *et al.* that La-substituted $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$) shows large remnant polarization, low synthesis temperature and good fatigue endurance [36]. Kim *et al.* has reported that the substitution of Nd^{3+} ions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films was more effective in improving the ferroelectric properties than La-substitution [37]. Mao *et al.* has also reported that substitution of Nd^{3+} ions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, ($\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$, $x = 0$ to $x = 0.09$) improved the ferroelectric and dielectric properties by suppressing the oxygen vacancies [38]. Tomar *et al.* reported that the substitution of Nd^{3+} and Sm^{3+} in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ as $\text{Bi}_{4-x}\text{M}_x\text{Ti}_3\text{O}_{12}$, ($\text{M} = \text{Nd}, \text{Sm}$) has improved the ferroelectric properties by reducing the leakage current [39]. Shigyo *et al.* has used Sm^{3+} ion in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and improved the dielectric and ferroelectric properties by suppressing the concentration of oxygen vacancies [40]. Noguchi *et al.* has uses vanadium ions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and achieve remnant polarization ($2P_r$) of over $40 \mu\text{C}/\text{cm}^2$ without compensating other physical properties [41].

From the above discussions, it has been concluded that substitution of La, Nd, Sm, Gd, Dy, and V were improving the ferroelectric and magnetic properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by suppressing the concentration of oxygen vacancies and reducing the conduction losses. In this context Paul *et. al.* in 2014 studied the multiferroic and magnetoelectric properties of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Fe}_x\text{O}_{12\pm\delta}$, $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12\pm\delta}$ and $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Ni}_x\text{O}_{12\pm\delta}$ ceramics [42-44]. They have found that the substitution of Sm at Bi-site and substitution of Fe, Co, and Ni at Ti-site improved the ferroelectric, ferromagnetic as well as magnetoelectric coupling of the ceramic compounds. The authors have used solid state reaction method to fabricate the compounds and proposed the F-center exchange mechanism and super-exchange interaction mediated through bridging oxygen to explain the source of ferromagnetism in ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Up to these findings, only single dopant at Ti-site has been investigated to enhance the multiferroic and magnetoelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. On the similar framework, multi dopants have been used subsequently to improve the multiferroic properties of Aurivillius based compounds.

Extending our discussion on multi dopants systems, Jun Xiao et al. in 2015 has worked on four layered structured ferroelectrics on Ni-doped $\text{Bi}_4\text{NdTi}_3\text{Fe}_{1-x}\text{Ni}_x\text{O}_{15}$ ($x=0.1, 0.3, 0.5$ and 0.7) ceramics. The ferroelectric and magnetic properties together the optimum room temperature multiferroic property was acquired for $x=0.3$ composition [45]. In the same year Ruixia Ti et al. has worked on $\text{Bi}_{3.25}\text{La}_{0.75}(\text{Ti}_{3-x}\text{Fe}_{x/2}\text{Co}_{x/2})\text{O}_{12}$ ($0 \leq x \leq 0.5$) polycrystalline ceramics synthesized by the conventional solid state reaction method. The ceramics with $x = 0.25$ composition possess the best properties, including phase purity, large ferroelectric polarization and remnant magnetization compared with other samples [46]. In the year 2017, the D. L. Zhang et al. reported the structure evolution, magnetic and ferroelectric properties in Co-doped four and three-layered intergrowth Aurivillius compounds $\text{Bi}_4\text{NdTi}_3\text{Fe}_{1-x}\text{Co}_x\text{O}_{15}$ - $\text{Bi}_3\text{NdTi}_2\text{Fe}_{1-x}\text{Co}_x\text{O}_{12-\delta}$ [47].

In continuation of this work, Yuying Wu et al. in 2017 and Ruixia Tia et al. in 2019 have synthesized $\text{Bi}_{4.25}\text{Gd}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$ and $\text{Bi}_4(\text{Ti}_{3-x}\text{Fe}_{x/2}\text{Co}_{x/2})\text{O}_{12}$ ($0 \leq x \leq 0.4$) polycrystalline ceramics. The low temperature ferromagnetism is successfully induced by Fe/Co co-doping. Particularly, the $x=0.3$ ceramics possess the largest remnant magnetization ($2M_r$) of about 0.272 emu/g at 100 K [48, 49].

From the existing literature on multiferroicity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, it has been concluded that the research on Aurivillius based structured ferroelectric compounds is the burning topic amongst the scientific community all around the world. The search has been going on to synthesize new class of materials and to enhance the multiferroic as well as magnetoelectric coupling of the existing Aurivillius based compounds for the futuristic applications.

Now we are concentrating our discussions on some of the characteristic properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ based Aurivillius compounds investigated by different researchers, so that readers have some basic understanding, that how the substitutions at A- and B-sites affect the structural, multiferroic and magnetoelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound.

6. Structural studies of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

The pure and substituted samples of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ multiferroic ceramics were mostly synthesized by solid state reaction method by different authors. Generally, high purity oxide precursor materials have been used to synthesize $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The sintering temperature were varied from 850°C to 1100°C depending upon the dopant used. Chen *et al.* [34] have first time synthesized the $\text{Bi}_4(\text{Ti}_1\text{Fe}_2)\text{O}_{12-\delta}$ multiferroic ceramics using solid state reaction method. They have found single phase material with no impurity peaks. The lattice parameters and the unit cell volume were found to increases with substitution, which may be attributed to the larger radius of Fe^{3+} ions (0.0645 nm) in

comparison to Ti^{4+} ions (0.0605 nm). J. Paul et al. have substitute the Sm^{3+} ions at Bi-site and Fe/Co/Ni ions at Ti-site in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. They found that, in case of Fe substitution, Fe_2O_3 replaces Ti-sites successfully without forming any impurity phase up to $x \leq 0.3$ composition, whereas, for $x > 0.3$, the structure of the system changes from orthorhombic to tetragonal [42]. On the other hand, in the case of Co and Ni doping, the optimum point of Co_3O_4 and NiO in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is $x = 0.07$. For $x > 0.07$ the Co_3O_4 and NiO will start forming the secondary phase in the system [43, 44]. The X-ray diffraction pattern of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12}$ has been shown in Figure 4. Upto $x=0.07$, the pure phase is obtained while at $x > 0.07$, an impurity peak at around $2\theta = 27.89^\circ$ (indicated by *) has been obtained, which can be attributed to the formation of secondary phase and is identified as bismuth cobalt oxide ($\text{Bi}_{25}\text{CoO}_{40}$).

Similar results have been observed in X-ray diffraction studies by Ruixia Ti et al. [46], where the authors observed the impurity peaks in Fe/Co co-doped $\text{B}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramic system. They have observed weak impurity peaks related to $\text{Bi}_2\text{Ti}_2\text{O}_7$ (for $x=0.01$) and Bi_2O_3 (for $x=0.05$). These impurity peaks were attributed to the evaporation of Bi during the high temperature sintering and non-stoichiometry induced by doping. The orthorhombicity defined by the formula, $2(a-b)/(a+b)$, where a and b are the lattice parameters was found to decrease with increasing substitution. Similar results have also been obtained for other bismuth layered structured compounds [47, 48].

Figure 4: X-ray diffraction pattern of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12}$ (Reprinted from reference [43] with kind permission from Springer Nature).

From the findings of X-ray diffractions studies, it has been concluded that the substituent used has altered the structure of the parent Bi-layered compounds. The occurrence of the impurity peaks will be dependent on the ionic radii of the dopant at A- and B-sites, the composition, the reactivity of the dopant with the other precursor materials and the sintering temperature also.

To study the structure of the synthesized compounds Raman spectroscopy is a very useful technique and frequently used to investigate the structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and related compounds. It has been published in different reports that orthorhombic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has 24 Raman active modes [50, 51]. The Raman spectra of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12}$ has been shown in Figure 5. The low frequency modes i.e., modes observed below 200 cm^{-1} are ascribed to the vibrations of Bi^{3+} ions in the perovskite layer, while the high frequency modes above 200 cm^{-1} are attributed to the bending and stretching of TiO_6 octahedra.

In Figure 5, the Raman modes were observed at around 116, 144, 224, 268, 328, 357, 535, 564, 610 and 850 cm^{-1} . It has been found that mode at 224 cm^{-1} is getting suppressed with increasing substitution of Co. This can be ascribed to the decrease in distortion of TiO_6 octahedra and hence the decrease in orthorhombicity [52]. The modes observed at 116 and 144 cm^{-1} reflects the vibration of Bi^{3+} ions in layer structured perovskite. The more fascinating result is the Raman mode at about 716 cm^{-1} , which becomes more prominent with increasing Co content. The occurrence of new Raman mode is ascribed to the vibration of Co-O bond, due to the substitution of Ti by Co ions whose intensity increases gradually with increase in Co substitution. This confirms the substitution of Co ions in perovskite unit cell.

Similar results of Raman spectroscopy have been observed for Fe/Co co-doped $\text{B}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics by Ruixia Ti et al. [46].

It has been reported that after co-doping of Fe and Co, the relative intensity of common modes decreases gradually. The bands observed at 269, 557, and 851 cm^{-1} becomes broader and could be attributed to the lattice distortion and stress induced by doping. A new vibration mode at 732 cm^{-1} comes into existence after doping, whose intensity increases with doping. The authors ascribed this new mode to the FeO_6 and CoO_6 octahedral.

Finally, from the structural studies, it has been concluded that the substitution at A-and B-site alter the crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The structure transforms from orthorhombic to tetragonal at some optimum compositions and the orthorhombicity decreases with substitution due to relaxation of orthorhombic distortions. It was confirmed from Raman studies that the intensity of common Raman active modes decreases, whereas new modes come into picture with substitution.

Figure 5: Raman Spectra of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12}$ (Reprinted from reference [43] with kind permission from Springer Nature).

7. Ferroelectric studies of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

Ferroelectrics are technologically important materials, for applications in non-volatile ferroelectric random-access memories (Fe-RAM). One of the characteristic properties of a multiferroic material is that it shows saturated polarization-electric field (P-E) hysteresis curve. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Aurivillius-type compounds are the promising candidates for such applications. These materials offer several advantages such as fatigue-free, lead free, low operating voltage and high curie temperature. The fatigue problem of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compound was resolved by the addition of different dopants (La, Nd, Sm, V etc.) at Bi^{3+} site, which suppresses the oxygen vacancies and improve the ferroelectric properties of the compound.

Figure 6 shows the room temperature P-E hysteresis curve of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12-\delta}$ ceramics. It was observed that the shape of ferroelectric loop improves with increasing content of Sm^{3+} and Co^{3+} ions, which indicate the reduction in conduction losses. With increase in substitution, there is significant enhancement in remnant polarization ($2P_r$) and its value increases from $8.66 \mu\text{C}/\text{cm}^2$ (for $x=0$) to $15.82 \mu\text{C}/\text{cm}^2$ (for $x=0.07$). This enhancement was attributed to the decrease in orthorhombicity which reduces the defects related to segregation of vacancies and enhances the movement of domain walls [53].

Similar results have also been observed for Fe, Ni and other co-doping systems at different concentrations [42, 44, 46]. One of the most important factors, that affect the ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, is how the grain size vary with dopant concentration. It was proposed that if the grain size increases with substitution, the volume fraction of grain boundaries reduces. This decreases the probability of trapping the space charge at the grain boundaries. As a result, the pinning of neighbouring domains gets reduced, which makes domain reorientation easier and enhances the remnant polarization [54].

It was concluded from ferroelectric studies that substitution of different ions at Bi-site has profound effect on the ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

Figure 6: Ferroelectric hysteresis loops of $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12-\delta}$ ($x = 0, 0.02, 0.05, 0.07$) (Reprinted from reference [43] with kind permission from Springer Nature).

8. Multiferroic studies of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

The co-existence of ferroelectricity and ferromagnetism are the pre-requisite of the multiferroic material. Multiferroic are of great technological potential, since ferroelectricity and ferromagnetism co-exist at room temperature in same phase. In $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ferromagnetism has been introduced by incorporating the partially filled d-orbitals elements such as Fe, Ni, Co, Mn, Gd, Cr etc. or their combination at the Ti^{4+} site.

Figure 7 shows the magnetization curve for $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12\pm\delta}$ ($x = 0, 0.02, 0.05, 0.07$) ceramics at room temperature.

Figure 7: Room temperature M - H curve for $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12\pm\delta}$ ($x = 0, 0.02, 0.05, 0.07$) ceramics (Reprinted from reference [43] with kind permission from Springer Nature)

It was observed from Figure 7 that for pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, an anti S-type nature of loop has been observed, which confirm the diamagnetic nature of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Whereas, with substitution of Sm and Co, the loop gradually changes into a S-type hysteresis loop, indicating the origin of weak ferromagnetism. The remnant magnetization was found to increase with increasing content of Co ions.

The authors have proposed different mechanism to explain the origin of weak ferromagnetism:

- i. In oxide materials the oxygen vacancies were created naturally to compensate the charge neutrality. In $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, when Ti^{4+} site is substituted by Co^{3+} ions, there is a formation of $\text{Co}^{3+} - \square - \text{Co}^{3+}$ network structure where ($\square$) denotes the oxygen vacancy). There is creation of F-centres, when an electron having a down spin trapped in between these vacancies [35, 55]. Subsequently, Co^{3+} have an unoccupied $3d^6$ spin orbital, so it might be possible that F-centre exchange mechanism is suitable in $\text{Co}^{3+} - \square - \text{Co}^{3+}$ network [56]. The direct ferromagnetic

coupling is possible through exchange interactions between the two neighbouring Co^{3+} ions via F-centre.

- ii. In another explanation, it was proposed that $\text{Co}^{3+}\text{-O-Co}^{3+}$ coupling might occur, which also leads to ferromagnetic state.
- iii. The valence state of Co ions also affects the existence of ferromagnetic state. Co ion may exist in +2 valence state also. This also favours the creation of $\text{Co}^{3+}\text{-O-Co}^{2+}$ network structure. Therefore, the existence of double exchange interactions also favours the ferromagnetic state in doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics [56].

Similar explanations have been given by Ruixia Ti et al. [46] in Fe/Co co-doped $\text{B}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics. It was reported by Ruixia Ti et al that, $x=0.1$ sample has nonferromagnetic properties, whereas ferromagnetic nature comes into existence for all other compositions. It was observed for $x=0.25$ sample, maximum remnant magnetization (M_r) and smallest saturation magnetization (M_s), or we can say that largest remnant magnetization ratio M_r/M_s was observed, which shows largest ferromagnetism in the considered sample.

The authors have proposed similar explanations for the observed ferromagnetism such as:

- i. Ferromagnetic interaction between bound magnetic polarons, and
- ii. Ferromagnetic double exchange interactions between different valence states of Fe and Co ions.

From the above discussions, it has been concluded that, it is possible to introduce the magnetic properties in ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and hence the multiferroism. Different mechanisms have been proposed to explain the origin of ferromagnetism in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

9. Magnetoelectric coupling in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

The magneto electric effect provides an additional degree of freedom for device fabrication. To determine the order of coupling between ferroelectric and ferromagnetic orders, magnetoelectric voltage is measured across the sample under applied dc magnetic field. The ME coupling co-efficient ($\alpha = dE/dH$), is calculated from the output voltage [57]. The variation of α as a function of applied dc magnetic field (H_{dc}) at room temperature is shown in Figure 8 for $\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_3\text{O}_{12-\delta}$ ($x = 0.02, 0.05$ & 0.07).

From Figure 8, it has been observed that the coupling coefficient has nonlinear behaviour with the applied dc magnetic field. The α is also observed to increase with increase in substitution. These results confirm the coupling between two ferroic orders. The coupling between two different ferroic orders is attributed due to the interaction between sub-

lattices of electric and magnetic phases, through the transmission of stress and strain from one sub-lattice to another sub-lattice [58]. In the presence of magnetic field, the strain-induced magnetic sub-lattice induces a stress on the electrical sub-lattice which is realized as ME output.

Figure 8: The variation of Magnetolectric coefficient as a function of dc magnetic field (Reprinted from reference [43] with kind permission from Springer Nature)

Similar results have been observed by different authors, in Fe, Ni, Fe/Co co-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ compounds, which confirm the coupling between ferroelectric and ferromagnetic orders.

Finally, it would be concluded here that after substituting and optimizing the composition of substituents at A-site (Bi) and the B-site (Ti) in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, one can obtain the new class of multiferroic materials and the corresponding magnetoelectric coupling even at room temperature.

Table 1 gives the summary of different Aurivillius based compounds synthesized for possible applications as multiferroic materials.

Table 1: Summary of Aurivillius based compound synthesized for multiferroic applications.

S.No.	Type of Aurivillius Compound	Dopant Used	Year	Reference
1.	$\text{RBi}_4\text{FeTi}_3\text{O}_{15}$	$\text{R}=\text{Nd, Sm, Gd, and Dy}$	2003	[58]
3.	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	Partially substitution of Fe at Ti site	2008	[33]
4.	$\text{Bi}_4(\text{Ti}_1\text{Fe}_2)\text{O}_{12-\delta}$	Substituting Fe at Ti site	2010	[34]
5.	$\text{Bi}_4(\text{Ti}_1\text{Fe}_2)\text{O}_{12-\delta}$	Substituting Fe at Ti site	2010	[35]
6.	$\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Ni}_x\text{O}_{12\pm\delta}$	Substitution of Sm at Bi site and Ni at Ti site	2014	[44]
7.	$\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Co}_x\text{O}_{12\pm\delta}$	Substitution of Sm at Bi site and Co at Ti site	2014	[43]
8.	$\text{Bi}_{4-x}\text{Sm}_x\text{Ti}_{3-x}\text{Fe}_x\text{O}_{12\pm\delta}$	Substitution of Sm at Bi site and Fe at Ti site	2015	[42]
9.	$\text{Bi}_4\text{NdTi}_3\text{Fe}_{1-x}\text{Ni}_x\text{O}_{15}$	Substitution of Nd at Bi site and Ni/Fe at Ti site	2015	[45]
10.	$\text{Bi}_{3.25}\text{La}_{0.75}(\text{Ti}_{3-x}\text{Fe}_{x/2}\text{Co}_{x/2})\text{O}_{12}$	Substitution of La at Bi site and Fe/Co at Ti site	2015	[46]
11.	$\text{Bi}_4\text{LaTi}_3\text{FeO}_{15}$	Substitution of La at Bi site and Fe at Ti site	2015	[60]
12.	$\text{Bi}_4\text{NdTi}_3\text{Fe}_{1-x}\text{Co}_x\text{O}_{15}-\text{Bi}_3\text{NdTi}_2\text{Fe}_{1-x}\text{Co}_x\text{O}_{12-\delta}$	Nd at Bi site and Fe/Co at Ti site	2017	[47]
13.	$\text{Bi}_{4.25}\text{Gd}_{0.75}\text{Ti}_3\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{15}$	Gd at Bi site and Fe/Co at Ti site	2017	[48]
14.	$\text{Bi}_4(\text{Ti}_{3-x}\text{Fe}_{x/2}\text{Co}_{x/2})\text{O}_{12}$ ($0 \leq x \leq 0.4$)	Fe/Co at Ti site	2019	[49]

10. Future prospective of Aurivillius based multiferroic ceramics

Aurivillius based layered structured compounds have wide applications in ferroelectric random-access memories, high temperature piezoelectricity, photocatalytic applications and many more. From the technological point of view, the fabrication of Aurivillius based single-phase multiferroic materials, having applications at room temperature, is a complicated task. Various efforts are being made in this direction. The outcome of various research has confirmed that newly synthesized systems exhibit both the ferroelectric and ferromagnetic orders simultaneously, and these orders are coupled to each other at room temperature. Moreover, the ME coupling in Aurivillius based ceramic systems is small, and more efforts are required to enhance the ME coupling at room temperature, so that further applications can be extracted from the material. The room temperature single-phase multiferroic materials may definitely be used for the fabrication of data storage devices, multiple-state memory elements and sensors.

Moreover, in case of Aurivillius compounds, the requirement of high coercive field can make tough the required poling which is a disadvantage for the potential applications for these materials. The fabrication of thin films can overwhelm this problem, and enhances the applicability for Bi-based Aurivillius compounds. By reducing the thickness of the material, less voltage is required to apply high electric field, which enhances its utility in microelectronic devices. The ferroelectric properties in Aurivillius based thin films are studied well in the literature for optical applications. The growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin film depends on various parameters such as microstructure, orientation, and composition of the grown thin films. The substrate also plays an important role for optimizing the properties of the thin films. In the field of multiferroic thin films of Aurivillius based compounds, there are very less reports in the literature. The growth of Aurivillius based multiferroic thin films and their mechanism involved, is a burning topic amongst the scientific community. Different thin film techniques such as sol-gel spin coating, pulse laser deposition, and Magnetron sputtering can be used and optimized for the growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ based multiferroic thin films for futuristic applications.

11. Comparison of multiferroic and ferrite materials

Multiferroic materials are those, that exhibit two or more than two orders, including electric, magnetic, and elastic. Electric order originates from the ordering of electric dipoles, and magnetic order results due to the exchange interactions between the magnetic dipoles. Multiferroic materials have many potential applications in multifunctional devices such as multiple-state memory elements, transducers, spintronics, sensors, and terahertz radiations Bi-based Aurivillius-type oxides system having layered perovskite structure, attracted increasing research interest due to their wide applicability.

The existence of simultaneous electric and magnetic ordering at room temperature, makes this compound a good candidate for multiferroic applications. This Aurivillius-type oxides family can accommodate different elements at A- and B-sites and exhibit a rich spectrum of properties which enables the fabrication of new functionalized devices.

On the other hand, ferrites are oxides materials with outstanding magnetic properties. They are composed of iron oxide as main constituent and metal oxides. On the basis of crystal structure, ferrites are classified into: (i) Spinel ferrite, (ii) Garnet, (iii) Orthoferrite and, (iv) Hexagonal ferrites. They have broad range of industrial applications as high and low frequency transformer cores, electromagnetic interference (EMI) suppressions, antenna rods, core of coils in microwave frequency devices, computer memory core elements etc. These broad ranges of applications are owed to their low eddy currents, high resistivity, high saturation magnetization, and high Curie temperature. Moreover, ferrite nanoparticles have extraordinary chemical and physical properties, which has extended their scope in magnetically driven drug delivery system, MRI, and hyperthermia applications.

The main issue in single phase multiferroic materials is their low magnetoelectric coupling. To overcome this issue, lot of research has been carried out on multiphase multiferroic composites. The results shows that multiphase multiferroic composites have large value of saturation magnetization and polarization in comparison to single phase multiferroic systems. Composite's nanostructure is a good approach in this direction. Some of the composite system studied are $\text{NiFe}_2\text{O}_4\text{-BaTiO}_3$, $(\text{Ni, Zn}) \text{Fe}_2\text{O}_4\text{-BaTiO}_3$, $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$, $(\text{Ba, Sr}) \text{TiO}_3\text{-(Ni, Zn) Fe}_2\text{O}_4$ etc. [60-64]. Large number of applications can be extracted from the composite systems consisting of ferrite as one phase and ferroelectric as second phase. We can fabricate multiferroic composite using different single and mixed ferrites for magnetic properties and doped Bi-based Aurivillius compounds for ferroelectric properties. While designing multiferroic composites, parameters such as difference in thermal expansion, mismatch in crystal lattices and grain boundary has to be taken care.

Conclusions

In this chapter, authors have tried to give an overview of multiferroic materials their types and magnetoelectric coupling. Then, authors have included the work done so far on Aurivillius based multiferroic material ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) and discussions on its properties. At the end authors have incorporate comparison between ferrites and multiferroic materials and their future prospective.

Conflict of Interest

The authors declare that they have no conflict of interest.

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