

Structure and Properties of Manganese–Substituted Bismuth Titanates

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Abstract. Partial substitution of manganese for titanium in bismuth titanate is a potential method to introduce ferromagnetic properties to ferroelectric bismuth titanate. We have established that manganese-substituted bismuth titanate forms only at low manganese contents. As the manganese content is increased, secondary phases form. A combination of neutron and synchrotron X-ray powder diffraction has been used to determine the structure of manganese-substituted bismuth titanates with chemical composition $\text{Bi}_4\text{Mn}_x\text{Ti}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 1$ at 0.05 steps). Measurements between 4 K and 1073 K have been used to examine the phase transitions that they undergo. It was found the substitution of manganese into bismuth titanate increases the phase transition temperature to tetragonal by about 100 °C. Neutron diffraction and bulk magnetic susceptibility measurements demonstrate the absence of long-range magnetic cation ordering in selected examples.

1. Introduction

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is a well known ferroelectric material that has been extensively studied as a consequence of its potential commercial applications in non-volatile memories and electro-optical devices. The ferroelectric polarisation is a result of the interaction between the d^0 Ti^{4+} cation, the $6s^2$ lone pair electrons from bismuth Bi^{3+} in the “ Bi_2O_2 ” layer and the bridging O^{2-} anion, Figure 1 [1].

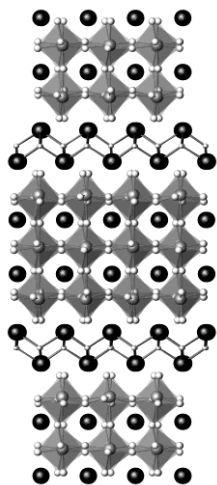


Figure 1. A schematic diagram of the Aurivillius oxide $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The black spheres denote bismuth and the white spheres denote oxygen. Bi–O bonds are drawn within the “ Bi_2O_2 ” layers and the titanium cations are contained by the octahedrons representing TiO_6 units.

The “ $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ ” perovskite block in bismuth titanate offers the possibility of substitution by transition metals, such as manganese. Such substitution is an avenue to introduce magnetism to

ferroelectric bismuth titanate and could result in a multiferroic material. Multiferroic materials are rare due to the usually conflicting requirement for a structurally symmetrical environment for the d^n magnetic cations and a structurally distorted environment stabilised by a d^0 cation.

2. Experimental

The series $\text{Bi}_4\text{Mn}_x\text{Ti}_{3-x}\text{O}_{12}$, where $0 \leq x \leq 1$ at 0.05 intervals, was synthesised via a solid state reaction with a maximum temperature of 950 °C. For the $x = 0, 0.10, 0.15$ and 0.20 , 10 g samples were prepared; 2 g samples were prepared for all other compositions. The reactions were monitored using Cu-K_α radiation on a Shimadzu X-6000 diffractometer.

Synchrotron X-ray powder diffraction data at $\lambda \approx 0.8 \text{ \AA}$ was measured at the Australian National Beamline Facility at the Photon Factory in Tsukuba, Japan [2]. Neutron diffraction patterns were measured for selected samples using the high resolution powder diffractometer Echidna at ANSTO's OPAL facility at Lucas Heights [3]. Rietveld refinements of the diffraction patterns were done using the program RIETICA [4]. Magnetic susceptibilities were measured using a Quantum Design Physical Property Measurement System.

3. Results and discussion

Figure 2 shows the series of diffraction patterns for $\text{Bi}_4\text{Mn}_x\text{Ti}_{3-x}\text{O}_{12}$ for $0 \leq x \leq 1$. Single phase samples were obtained for $x = 0, 0.05$ and 0.10 . At $x = 0.15$, peaks from $\text{Bi}_{12}\text{TiO}_{20}$ were first observed, with the most prominent peak at $d \sim 3.2 \text{ \AA}$. The intensity of these peaks increases with increasing manganese content. At $x = 0.55$, a $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ impurity was observed and this is seen to increase with increasing Mn contents. An example of a Rietveld refinement of the final compound in the series, $\text{Bi}_4\text{MnTi}_2\text{O}_{12}$ is shown in Figure 3. The diffraction pattern was refined using the three phases. While the parent $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ adopts a monoclinic structure, the monoclinic distortion is reasonably small [1]. Approximating the β angle to be 90° , an orthorhombic crystal system with space group $B2cb$ was used for the $\text{Bi}_4\text{MnTi}_2\text{O}_{12}$ phase.

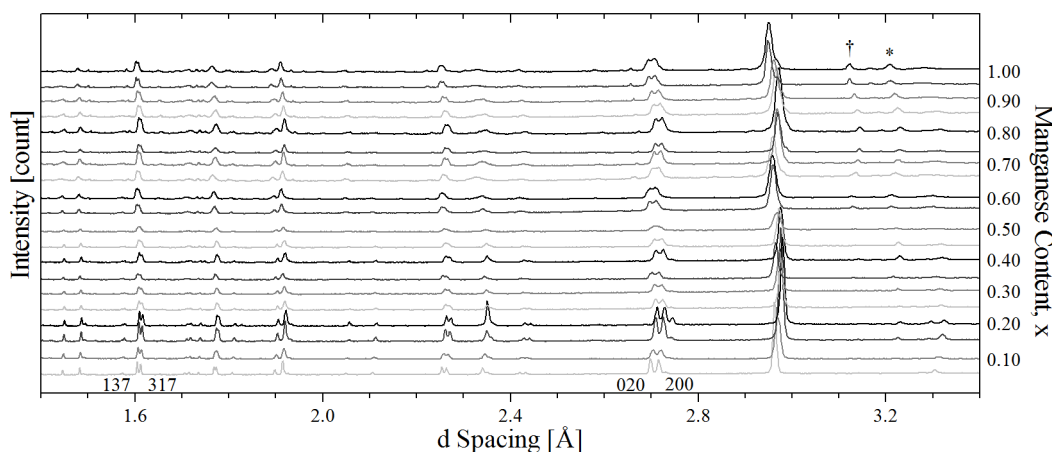


Figure 2. Portion of the diffraction patterns for $\text{Bi}_4\text{Mn}_x\text{Ti}_{3-x}\text{O}_{12}$ where $0.05 \leq x \leq 1.00$. The * indicate the peak due to $\text{Bi}_{12}\text{TiO}_{20}$ and † indicates the peak due to $\text{Bi}_2\text{Mn}_4\text{O}_{10}$.

Splitting of the orthorhombic 200/020 and 317/137 peaks at 2.7 \AA and 1.6 \AA respectively is evident in Figure 2 and 3. As the manganese content increases, the splitting of these peaks decreases, suggesting a shift to a tetragonal structure. This was not, however, achieved by $x = 1$ as evident in Figure 3.

Variable temperature synchrotron diffraction patterns were measured for the $x = 0.05$ and 0.50 samples. Both show a first order phase transition from orthorhombic $B2cb$ to paraelectric tetragonal $I4/mmm$ at 800 °C and 775 °C for $x = 0.05$ and 0.50 respectively, Figure 4 and 5. This compares to a temperature of $670\text{--}690 \text{ °C}$ found for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [5,6]. This suggests that manganese increases the phase transition temperature, but this may not be a linear effect.

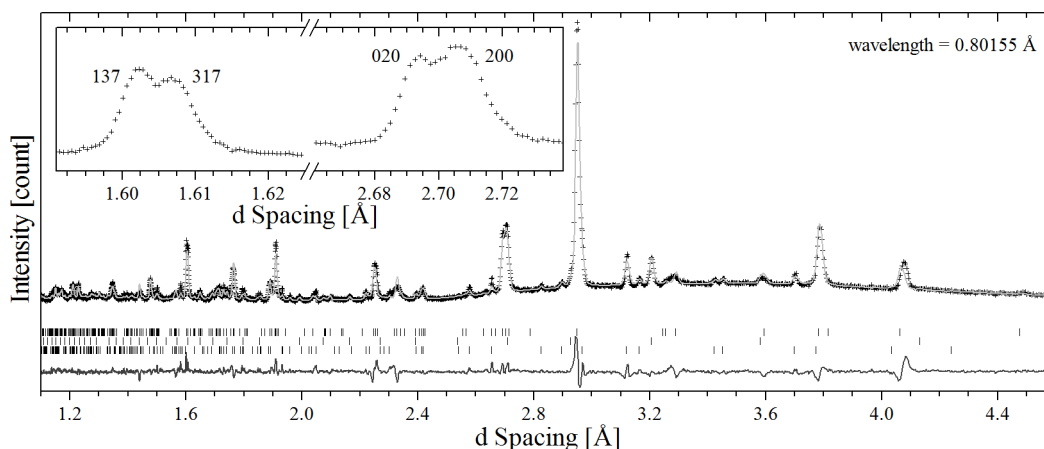


Figure 3. The Rietveld refinement of $\text{Bi}_4\text{MnTi}_2\text{O}_{12}$ using 3 phases. The first phase is orthorhombic $B2cb$ $\text{Bi}_4\text{MnTi}_2\text{O}_{12}$ 72.1(7) wt%, the second is $\text{Bi}_{12}\text{Ti}_{20}$ 7.62(2) wt% and the third phase is $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ 20.3(4) wt%. Inset, the resolved 200/020 and 317/137 peaks.

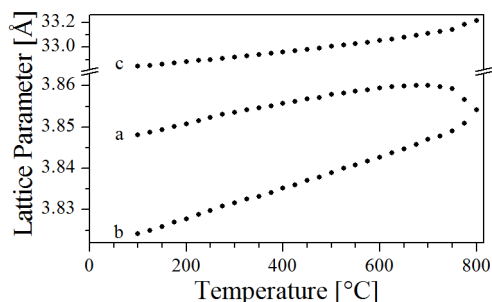


Figure 4. The lattice parameters for $\text{Bi}_4\text{Mn}_{0.05}\text{Ti}_{2.95}\text{O}_{12}$.

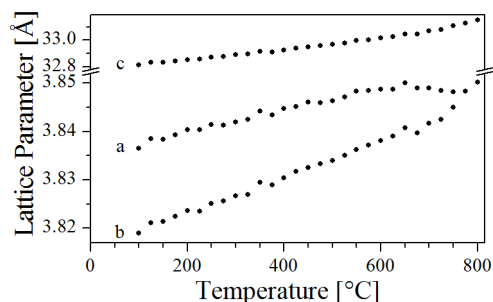


Figure 5. The lattice parameters for $\text{Bi}_4\text{Mn}_{0.50}\text{Ti}_{2.50}\text{O}_{12}$.

The inverse susceptibility against temperature for $x = 0.15$ is given in Figure 6 and the magnetisation against magnetic field is in Figure 7. No evidence for magnetic exchange was observed for this or the $x = 0.10$ sample, reflecting the small amount of manganese in these compounds. Higher values of x were not examined due to the existence of impurity phases.

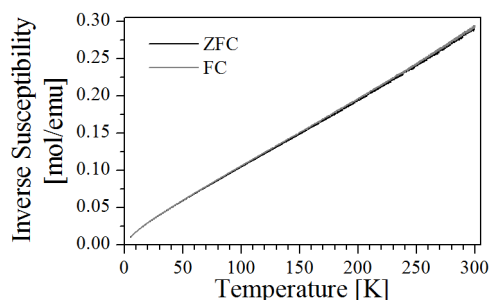


Figure 6. Inverse molar susceptibility for $\text{Bi}_4\text{Mn}_{0.15}\text{Ti}_{2.85}\text{O}_{12}$.

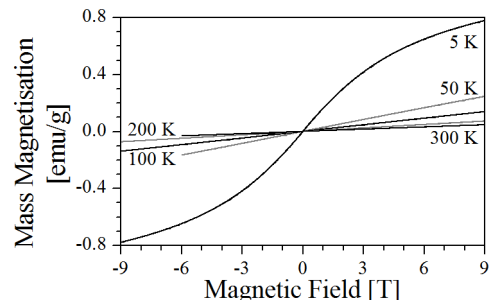


Figure 7. Magnetisation as a function of magnetic field for $\text{Bi}_4\text{Mn}_{0.15}\text{Ti}_{2.85}\text{O}_{12}$.

A comparison of the neutron diffraction pattern for $x = 0.20$ at 3 K and 300 K is in Figure 8 and shows no evidence of any structural or magnetic transition, indicating the lack of magnetic ordering in the low manganese content materials. One of the advantages of neutron diffraction is the ability to provide accurate structural information. However, given the negative scattering lengths of both Ti and Mn, -3.438 fm and -3.73 fm respectively, establishing the ordering of manganese in the perovskite block is difficult. Examination of the metal–oxygen bond lengths and measuring the distortion of the Ti/MnO₆ octahedral units using equation (1) shows that the inner but not the outer octahedral units

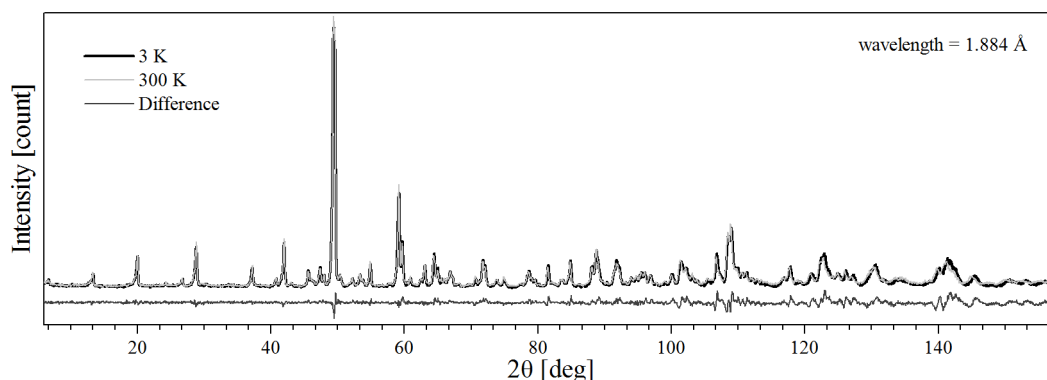


Figure 8. A comparison of the patterns for $\text{Bi}_4\text{Mn}_{0.20}\text{Ti}_{2.80}\text{O}_{12}$ collected at 3 K and 300 K. The 300 K pattern subtracted from the 3 K pattern is the difference profile.

become more symmetrical with the addition of manganese, Table 1 [7]. We propose that this is due to preferential occupancy by the manganese cations in the central octahedral units.

$$\Delta d = \frac{1}{6} \sum \left(\frac{M\text{-O}_{\text{obs}} - M\text{-O}_{\text{avg}}}{M\text{-O}_{\text{avg}}} \right)^2 \quad (1)$$

Table 1. Distortion of the Ti/MnO_6 octahedral units in the perovskite block.

	Outer	Inner
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	6.534×10^{-3}	2.318×10^{-3}
$\text{Bi}_4\text{Mn}_{0.10}\text{Ti}_{2.90}\text{O}_{12}$	6.324×10^{-3}	1.206×10^{-3}
$\text{Bi}_4\text{Mn}_{0.15}\text{Ti}_{2.85}\text{O}_{12}$	7.310×10^{-3}	0.412×10^{-3}
$\text{Bi}_4\text{Mn}_{0.20}\text{Ti}_{2.80}\text{O}_{12}$	6.708×10^{-3}	0.675×10^{-3}

4. Conclusion

The series of $\text{Bi}_4\text{Mn}_x\text{Ti}_{3-x}\text{O}_{12}$ $0 \leq x \leq 1$ was synthesised to study their magnetic properties in the anticipation that the introduction of magnetic cations into ferroelectric bismuth titanate would result in a multiferroic material. Synchrotron X-ray diffraction shows that only low manganese content samples are single phase. Increasing the Mn content produces $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_2\text{Mn}_4\text{O}_{10}$ as secondary phases and decreases the orthorhombic distortion. Variable temperature measurements also show an increase in the ferroelectric–paraelectric phase transition temperature by about 100 °C upon Mn doping. Magnetic susceptibility measurements of the single phase samples show a lack of long range magnetic ordering and this is supported by low temperature neutron diffraction. From changes in the distortion of the octahedra, we suggest that the Mn occupies the inner octahedral units of the perovskite block.

References

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