# Ferroelectric and dielectric properties of La/Mn co-doped $Bi_4Ti_3O_{12}$ ceramics*

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La/Mn co-doped $Bi_4Ti_3O_{12}$ ceramics, $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x$ = 0.02, 0.04, 0.06, 0.08), were prepared by the solid-state reaction method. The influence of manganese substitution for the titanium part in $Bi_{3.25}La_{0.75}Ti_3O_{12}$ on the sintering behaviour, microstructure, Raman spectra and electrical properties was investigated. The experimental results show that the phase composition of all samples with and without manganese doping, sintered at 1000 °C, consists of a single phase with a bismuth-layered structure belonging to the crystalline phase $Bi_4Ti_3O_{12}$. There is no evidence of any impurity phase, but a small change in crystallographic orientation is observed. The Curie temperature of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ceramics is steadily shifted to lower temperature with increasing Mn-doping content. Moreover, the remnant polarisation ($P_r$) of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ samples increases with Mn-doping content, and the $Bi_{3.25}La_{0.75}Ti_{2.92}Mn_{0.08}O_{12}$ sample exhibits the largest $P_r$ of 16.6 $\mu C/cm^2$.

**Keywords:** bismuth titanate, ceramics, doping, ferroelectric

**PACC:** 7780, 8120L, 8110J, 7780

## 1. Introduction

In recent years, with the increase in popularity of nonvolatile random access memories (NvRAMs), more and more attention has been paid to the study of ferroelectric materials. Lead zirconate titanate (PZT) is one of the most popular materials investigated for this use. However, there are some serious drawbacks in the commercial use of PZT, such as fatigue, imprint (loss of ability to write into the opposite state), and contamination of the environment.[1,2] On the other hand, bismuth layer-structured ferroelectrics have been recognized as promising materials for NvRAM applications due to their excellent fatigue-free nature and other electric properties.[3] Bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT), is a well-known member of this group of materials. It exhibits excellent performance for fast switching speed, high fatigue resistance with metal electrodes and good retention device owing to the large polarisation and almost fatigue-free behaviours.[4−9] In addition, its high Curie temperature (675 °C) makes it a suitable candidate for high temperature applications. Furthermore, the lead-free character of BIT is also an advantage for its use on a larger scale. However, the disadvantages of low remnant polarisation ($P_r$) and high coercive field ($E_c$) inhibit the application of BIT in the field of electronic devices.

Many researchers have suggested that ion substitution in BIT may be an effective approach to improve the ferroelectric properties of the materials. *A*-site and *B*-site substitutions have a significant effect on its ferroelectric properties. In the case of *A*-site substitution in BIT, by systematically studying lanthanides, such as La-, Pr-, Sm-, and Nd-substituted BIT films, Park *et al.*[10] reported that La-substituted BIT ($Bi_{3.25}La_{0.75}Ti_3O_{12}$, BLT) film has a large $P_r$, low processing temperature and fatigue-free characteristics. In the case of *B*-site substitution in BIT, some ions such as $V^{5+}$, $Nb^{5+}$ and $W^{6+}$ could effectively decrease the space charge density, resulting in an improvement in the ferroelectric properties.[11−13] According to the reported results, for the *A*-site-substituted BIT in both thin film and ceramic forms, the coercive field ($2E_c$) usually becomes larger than that of pure BIT, while for the *B*-site-substituted BIT,

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the 2 $E_c$ becomes smaller. These imply the fabrication of $A$- and $B$-site co-substituted BIT for the balance of $P_r$ and $2E_c$. Very recently, $A$- and $B$-site co-substituted BIT films, such as co-substitution of La and Mo, La and Zr, La and V, and Nd and W in BIT, were studied,[14−17] suggesting that $A$- and $B$-site co-substitution in BIT is an effective way to enhance the electrical properties. It was reported that Mn-doped $ABO_3$ perovskite ferroelectric thin films have shown excellent results in improving the ferroelectric properties, reducing the dielectric loss, enhancing the resistivity of the films, and increasing the dielectric tenability.[18−20] Recently, Zhong *et al.*[21] have studied the effect of Nd and Mn co-substitution on the properties of bismuth titanate films prepared by a chemical solution deposition technique; Kim *et al.*[22] have studied the effect of La and Mn co-substitution on the properties of bismuth titanate films by sol–gel processing. It is noted that these studies are concerned with the effect of doping with different ions on ferroelectric properties of BIT films, whereas there are no reports on the doping effect on BIT ceramics. In the present study, La/Mn co-doped BIT ceramics are prepared by a solid-state reaction technique. The effect of manganese on the sintering behaviour, Raman spectra, microstructure and electric properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ceramics is investigated.

## 2. Experimental

The starting materials used were reagent-grade $Bi_2O_3$, $TiO_2$, $La_2O_3$ and 99.0% pure $MnO_2$. The compositions of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ are denoted by BLTM02, BLTM04, BLTM06 and BLTM08 for $x$ equal to 0.02, 0.04, 0.06 and 0.08, respectively. The $Bi_{3.25}La_{0.75}Ti_3O_{12}$ sample was also prepared by the same method for comparison. For each compound, raw materials were weighed out according to the designed compositions and milled in absolute alcohol with agate balls for 24 h. The mixture was calcined at 800 °C for 5 h. To make BLTM ceramic samples, the calcined powders with binder were pressed into pellets at a pressure of 24 MPa and then sintered at 900 °C–1150 °C for 200 min.

Bulk densities of the sintered samples were determined by the Archimedes method. To investigate the crystallographic structures, x-ray diffraction (XRD) patterns of the ceramic samples were recorded over a 10°–70° ($2\theta$) range using a Philips diffractometer with Cu K$\alpha$ radiation. To study the surface morphology and microstructure of the samples, a field-emission scanning electron microscope (SEM) was used. Local structural changes within materials were detected using a JY LabRam HR800 raman microscope. To investigate the electrical properties, Ag electrodes were coated onto the polished surface of BLTM ceramic samples. Dielectric properties were measured at a frequency of 1 MHz by an impedance analyser (HP4192A). The ferroelectric polarisation property was recorded by a ferroelectric hysteresis measurement tester (ZT-I).

## 3. Results and discussion

XRD patterns of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x$ = 0, 0.02, 0.04, 0.06, 0.08) ceramic samples, sintered at 1000 °C, are shown in Fig. 1(a). It can be found that the phase composition of all samples, with and without manganese doping, consists of a single phase with a bismuth-layered structure belonging to the crystalline phase $Bi_4Ti_3O_{12}$. There is no evidence of any impurity phase, but a small change in crystallographic orientation is observed, i.e., the relative intensity of (00$l$) to (117) peaks decreases as the Mn-doping concentration increases. The intensity ratio of $I_{(006)}/I_{(117)}$ peaks varies from 0.72 to 0.21 as the Mn-doping content increases from $x = 0$ to $x = 0.08$ in $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ceramics. Figure 1(b) shows the XRD pattern of the BLTM08 sample sintered at temperatures in the range of 900 °C–1150 °C. At low sintering temperature (900 °C), relatively weak peaks are observed for the BLTM08 sample, implying low crystallinity. As the sintering temperature rises, the XRD peaks become sharpened, indicating a growth in crystallinity with increasing temperature. However, as the sintering temperature increases to 1150 °C, there are some other weak diffraction peaks in the XRD pattern, which could not be found in the XRD patterns sintered at other low temperatures, indicating the existence of some impurity phases. These impurity phases may be related to a strong volatilisation of bismuth at high temperatures.

The densification behaviour of BLTM ceramic samples sintered at different temperatures ranging from 900 °C to 1150 °C is shown in Fig. 2. For BLTM08, the bulk density increases with the increase in temperature from the lowest at 900 °C to the maximum value at 1100 °C and then reduces abruptly at 1150 °C. The variations in relative density with the sintered temperature for BLTM02, BLTM04, and BLTM06 compositions show similar tendencies to that for BLTM08, but the maximum value of the relative

density of these three compositions occurs at 1050 °C, lower than that of BLTM08. It is noted that the maximum values of relative density of BLTM samples increase with the increase in Mn-doping content in the composition. As shown in Fig. 2, BLTM06 has the highest theoretical density among the three samples, and its density reaches 98.6%. It is obvious that the sintering behaviour of BLTM could be influenced by adding even a small amount of manganese in the composition.

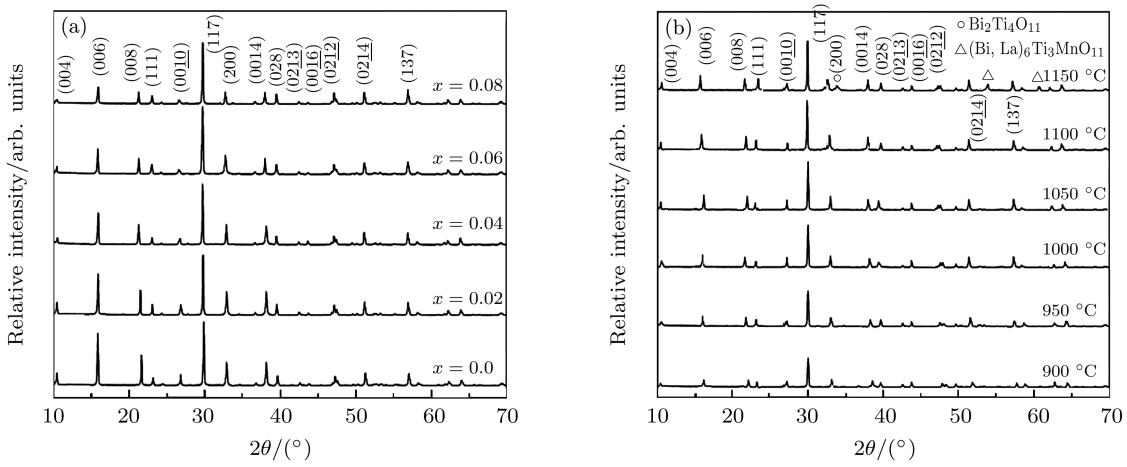



**Fig. 1.** (a) XRD patterns of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x$ = 0, 0.02, 0.04, 0.06, 0.08) samples sintered at 1000 °C, (b) XRD patterns of BLTM08 sample sintered at temperatures in the range of 900 °C–1150 °C.

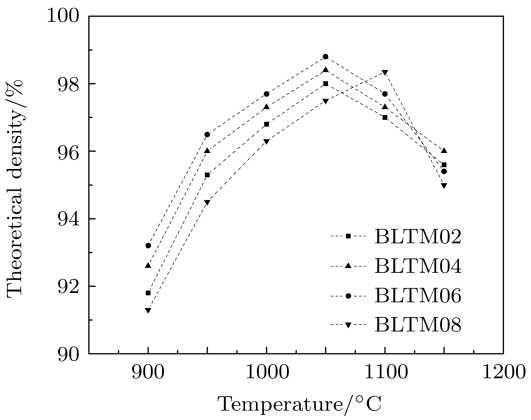



**Fig. 2.** Densification behaviour of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x$ = 0.02, 0.04, 0.06, 0.08) ceramics sintered at different temperatures.

Since the ionic radius of $Mn^{4+}$(0.53 Å) is smaller than that of $Ti^{4+}$(0.61 Å), and that of $La^{3+}$(1.032 Å) is almost equal to that of $Bi^{3+}$(1.03 Å), it might be reasonable that $Mn^{4+}$substitution, compared with the $La^{3+}$ substitution, will lead to larger changes of lattice parameter. BLTM samples sintered at the temperature at which maximum density is obtained are used for the measurement of lattice parameter. The variations of lattice parameters$a$, $b$ and $c$ for samples, calculated according to the XRD patterns, are shown in Fig. 3. We can see that the in-plane lattice constant, $a$, decreases while $b$ increases with manganese doping, resulting in a decrease in the orthorhombicity defined as $2(a-b)/(a+b)$,[23] from $8.71\times10^{-3}$ to $2.66\times10^{-3}$ as the Mn-doping content increases from $x = 0$ to 0.08 in BLTM ceramics. The decrease in the orthorhombicity suggests that the relaxation of the structural distortion should come from the substitution.

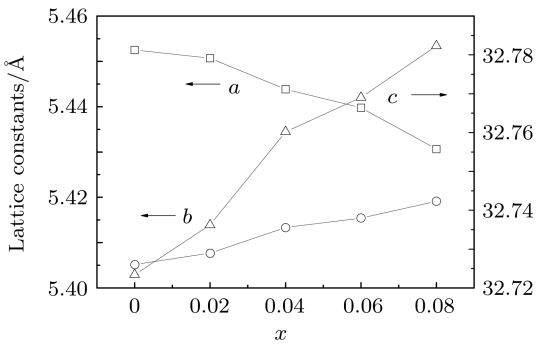



**Fig. 3.** Variation of lattice parameters $a$, $b$ and $c$ for BLTM samples at maximum density.

Figures 4(a)–4(d) show SEM micrographs of the sintered BLTM samples with different Mn-doping contents at the temperature corresponding to the maximum density. As can be seen in Fig. 4, the grain sizes of BLTM ceramics increase gradually with increasing Mn-doping content in BLT.

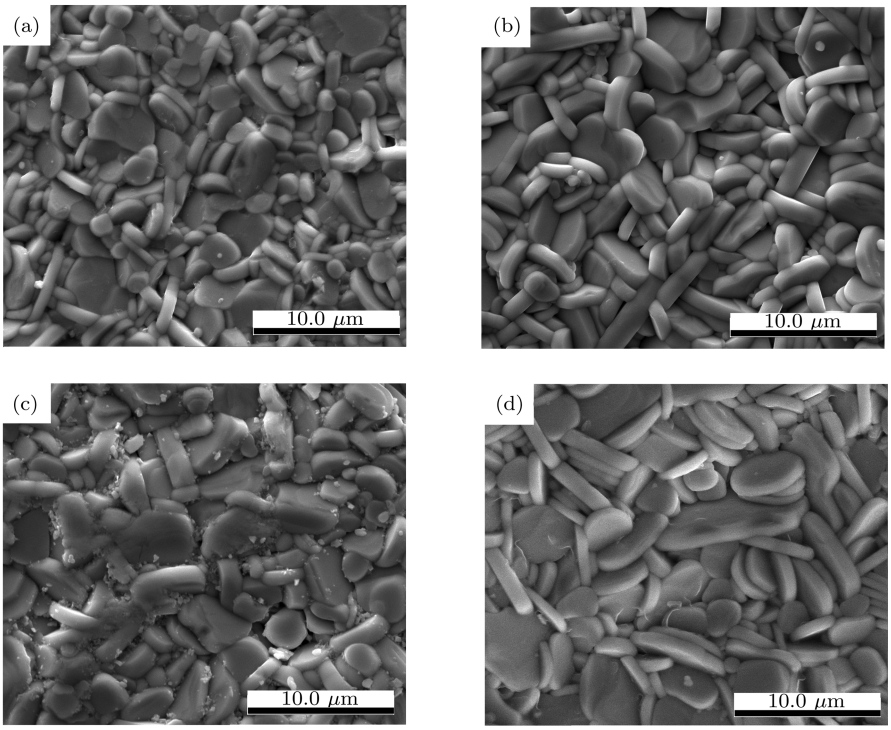



**Fig. 4.** SEM micrographs of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ samples for (a) $x = 0.02$, (b) $x = 004$, (c) $x = 0.06$, and (d) $x = 0.08$.

Raman scattering has proved to be a valuable technique to gain information about local structures in materials. The Raman spectra of the BLT, BLTM02, BLTM04, BLTM06, and BLTM08 samples sintered at 1000 °C are shown in Fig. 5. Here, we also give the Raman spectrum of pure BLT for comparison. It was reported that the active modes of Raman spectra of BIT were at 226 $cm^{-1}$ and 270 $cm^{-1}$ assigned to the internal angle Ti–O bending vibrations of $TiO_6$ octahedron; 348 $cm^{-1}$ to the combination of stretching and bending vibrations; and 850 $cm^{-1}$ to the stretching vibrations.[24–26] As shown in Fig. 5, the Raman spectra of BLTM samples with various Mn-doping contents are very similar, indicating that the BIT structure is well kept in the BLTM samples. The Raman results are in very good accordance with those of XRD.

Raman mode at about 706 $cm^{-1}$ increases with the increase in Mn-doping content. The frequency of the new Raman mode is in accordance with that of the high-frequency phonon band of the octahedron with $A_{1g}$ symmetry.[27] So, it is reasonable to speculate that the new Raman mode resulting from the Mn–O vibrational mode is due to the substitution of Ti by Mn in the $TiO_6$ octahedron. The gradual enhancement of the new Raman mode with the increase in Mn-doping content further confirms the Mn substitution at the $B$ site in BLTM ceramic samples.

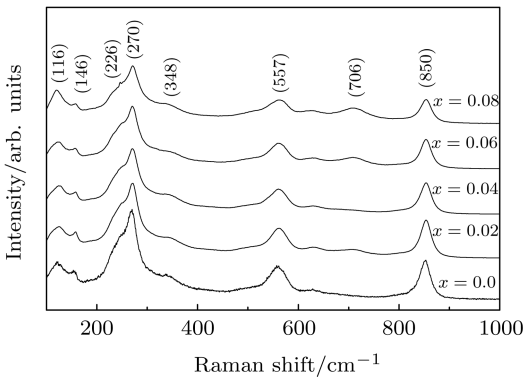



**Fig. 5.** Raman spectra of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x =$ 0, 0.2, 0.4, 0.6, 0.8) samples.

BLTM samples sintered at the temperature for maximum density values are used for the measurement of dielectric property. Figure 6 shows the temperature dependences of the dielectric constant and loss of BLTM02, BLTM04, BLTM06, and BLTM08 ceramics measured at a frequency of 1 MHz. It is found that the Curie temperature ($T_C$) of BLTM decreases

with increasing Mn-doping content. The Curie temperature ($T_C$) of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x$ = 0.2, 0.4, 0.6, 0.8) samples are 351, 345, 339, and 334 °C for BLTM02, BLTM04, BLTM06, and BLTM08 respectively (see Table 1), which are lower than the $T_C$ (355 °C) for BLT ceramic with the same amount of La doping. Such a decrease in $T_C$ of Mn-doped bismuth layer-structured ceramics can be explained as follows.

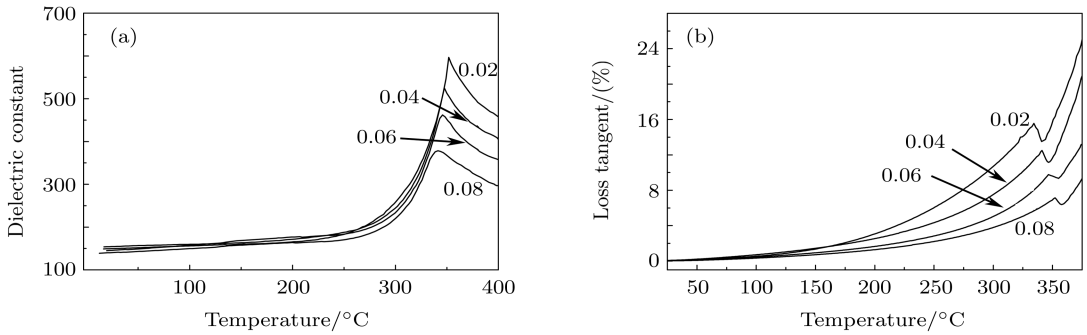



**Fig. 6.** Temperature dependence of (a) dielectric constant and (b) loss tangent of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ ($x$ = 0.2, 0.4, 0.6, 0.8) samples.

It can be seen from Fig. 3 that the lattice constant $a$ decreases continuously with increasing Mn-doping content, whereas the value of $b$ increases. As a result, the difference between $a$ and $b$ becomes increasingly small for the samples with increasing Mn-doping content, and the crystal structure symmetry increases continuously. It is the increase in crystal structure symmetry that leads to a decrease in the Curie temperature of BLTM. The decrease in Curie temperature with an increase in its crystal structure symmetry has been well documented in the literature for $BaTiO_3$-based ferroelectrics as well.[28,29] For instance, it was reported that as the $c/a$ ratio of tetragonal $BaTiO_3$ decreased towards unity with the doping of $Sr^{2+}$, $Sn^{4+}$ or $Zr^{4+}$, its Curie temperature shifted to lower temperatures. In contrast, the substitution of $Pb^{2+}$ for $Ba^{2+}$ in tetragonal $BaTiO_3$ led to an increase in both the $c/a$ ratio and Curie temperature.

It is also noted that the peaks of dielectric constants at Curie temperature becomes broadened when the composition contains a larger amount of manganese. This phenomenon indicates the existence of a diffuse-type ferroelectric phase transition, as found in other ferroelectric ceramics.[30] In addition, the loss tangents of BLTM ceramics are lower than that of pure BIT reported in Ref. [31].

Figure 7 shows the ferroelectric hysteresis loops of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ samples with various Mn-doping contents of $x$ = 0.04–0.08. As shown in Fig. 7, the remnant polarisation increases with increasing Mn-doping content. Such an increase in $P_r$ of Mn-doped bismuth layer-structured ceramics can be explained as follows.

Firstly, as we know, $Bi_4Ti_3O_{12}$ has a strong anisotropy of polarisation which is as small as 4 $\mu C/cm^2$ along the $c$-axis, but is very large (50 $\mu C/cm^2$) along the $a$-axis. As the Mn-doping concentration increases, the relative intensity of ($00l$) peaks to that of the (117) peak decreases. This means that the relative density of grains with $c$-axis orientation decreases while that of grains with other orientations, such as $a$-axis orientation, increases.

Secondly, Mn doping in BLT leads to a decrease in the orthorhombicity, which is expected to weaken the segregation of defects at domain walls and speed up the movement of the domain walls.[32]

Thirdly, as shown in Fig. 4, the grain sizes of BLTM ceramics increase gradually with increasing Mn-doping content in BLT. It is generally accepted that space charges may decrease the ferroelectric properties by trapping at grain boundaries and pinning the neighbouring domains. With the increase in Mn-doping content, the increase of grain size would decrease the grain boundary proportion and therefore decrease the probability of space charge trapping at grain boundaries.

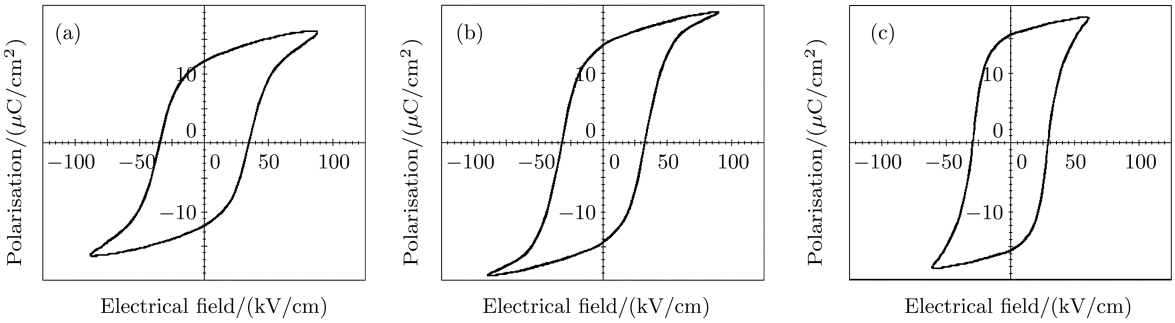



**Fig. 7.** Ferroelectric hysteresis loops of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ samples for (a) $x = 0.04$, (b) $x = 0.06$, and (c) $x = 0.08$.

The remnant polarisation ($P_r$) and coercive field ($2E_c$) of BLTM samples are listed in Table 1. Although the values of $P_r$ obtained in the present work are a little lower than that of $Bi_{3.25}La_{0.75}Ti_{2.97}Mn_{0.03}O_{12}$ film prepared by the sol–gel method (18 $\mu C/cm^2$), its $2E_c$ is much lower than that of $Bi_{3.25}La_{0.75}Ti_{2.97}Mn_{0.03}O_{12}$ film (200 kV/cm).[33] In addition, the coercive field ($2E_c$) of $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ samples decreases continuously with increasing Mn-doping content, as found in other $B$-site substitution BIT ceramics.[34]

**Table 1.** Curie temperature ($T_C$), remnant polarisation ($P_r$), and coercive field ($2E_c$) of BLTM ceramics.

| BLTMx | 0.02 | 0.04 | 0.06 | 0.08 |
|---|---|---|---|---|
| $T_C/°C$ | 351 | 345 | 339 | 334 |
| $P_r/(\mu C/cm^2)$ | 10.2 | 12.0 | 14.2 | 16.6 |
| $2E_c$/(kV/cm) | 78.4 | 72.6 | 66.4 | 57.2 |

# 4. Conclusion

La/Mn co-doped $Bi_4Ti_3O_{12}$ ceramics (BLTM) have been prepared by a solid-state reaction technique. The influence of Mn-substitution for the Ti part in $Bi_{3.25}La_{0.75}Ti_3O_{12}$ on the sintering behaviour, microstructure, Raman spectra and electrical properties was investigated. It was found that:

(A) When sintered at 1000 °C, the phase composition in all samples with and without Mn doping consists of a single phase with a bismuth-layered structure belonging to the crystalline phase $Bi_4Ti_3O_{12}$, but a small change in crystallographic orientation is observed.

(B) The Raman spectra of BLTM samples with various Mn-doping contents are very similar, indicating that BIT structure is well kept in our BLTM samples. Raman mode at about 706 $cm^{-1}$ increases with the increase in Mn-doping content. The frequency of the new Raman mode is in accordance with that of the high-frequency phonon band of an octahedron with $A_{1g}$ symmetry. The gradual enhancement of the new Raman mode with the increase in Mn content further confirms the Mn substitution at the $B$ site in BLTM ceramics.

(C) The Curie temperature of Mn-doped BLT is steadily shifted to lower temperature with increasing Mn-doping content. It is the increase in crystal structure symmetry that leads to a decrease in the Curie temperature of the samples.

(D) The remnant polarisation of BLTM samples increases with the Mn-doping content, which might be due to the modification in orientations of grains and the enhancement of grain size.

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