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Structural, Dielectric and Ferroelectric Properties of Manganese (Mn) Doped Bismuth Titanate ($Bi_4Ti_3O_{12}$) Ceramics

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Abstract— Manganese (Mn) doped Bismuth Titanate $Bi_4Mn_xTi_{(3-x)}O_{12}$ (x = 0.0, 0.1, 0.2, 0.3, 0.4) powders were prepared by high temperature solid state reaction route. Structural properties were studied by X-ray diffraction (XRD). Dielectric and ferroelectric properties were studied by making ceramic pellet samples. The dielectric constant ε_r and loss tangent (tan δ) of BMT ceramics were measured as a function of frequency (1 kHZ - 100 kHz) and were also studied the comparison of two temperatures (Room Temp and 50°C) applied with temperature controller. Hysteresis loop measurements were performed with Sawyer-Tower circuit at 100 kHz and 10 V. According to the results, ferroelectric hysteresis loops were changed with respect to stoichiometric compositions. According to the experimental results the laboratory prepared devices were utilized for nonvolatile ferroelectric random access memory (NVFRAM) applications.

***Keywords*- XRD, BMT, Hysteresis, Sawyer-Tower**

Introduction

FERROELECITY in $Bi_4Ti_3O_{12}$, also known as BIT, was described by Subbarao and Van Uitert in parallel works, and few year later Cummings described the monoclinic symmetry and polar domain structure in BIT [1]. After these initial works, the best known compound within the Aurivillius family, $Bi_4Ti_3O_{12}$, an attractive lead-free substitude for the materials commonly used in ferroelectric random access memory (FeRAM), and its crystal structure and ferroelectric properties have been extensively studied [2-4]. Nowadays, due to its large remanent polarization (P_r) low crystallization temperature and high Curie temperature, more than 70 compounds of this family are known and **more than 50 present ferroelectricity.** Ion substitution in the BIT is known to be an effective technique for improving its electrical properties, such as P_r and fatigue characteristics [5-12]. In this study, the effect of Mn contents on the crystal structure, dielectric properties and memory behavior of BMT ceramics are systematically investigated.

2.EXPERIMENTAL PROCEDUERE

To prepare the manganese (Mn) doped bismuth titanate ($Bi_4Ti_3O_{12}$) powder, Bi_2O_3, MnO_2 and TiO_2 were used as starting materials. The purity of materials were 100%, 96.76% and 98.21% respectively. They were checked by EDXRF (EDX-700) and XRD spectroscopy. The powder was weighted on electronic balance (FEJ-200) to agree with the molar concentration of $Bi_4Mn_xTi_{(3-x)}O_{12}$ (x=0.0, 0.1, 0.2, 0.3 and 0.4) . And then they were mixed in a clean agated mortar and ground with a pestle for 3 hours each to form homogeneous. Later, sieve it with a mesh to become uniform grain size. The mixture of each powder was then placed in clean crucible and heat-treated at 1000˚C for 2 hours in air atmosphere with method of solid state reaction route. In addition, these samples were ground in a cleaned agate mortar and sieve them with a mesh secondly to be good fined powder. Then each BMT powder was added with polyvinyl alcohol PVA (organic binder solution) to design pellet forms with sample-making machine that weighs 5 tons and was put on each of them. A pair of copper electrode was attached to the pellets which were circular-shaped flat samples for more electrical contact. The diameter of each pellet was 1.35 cm and the area of that pellet was 1.4314 cm^2. The area of copper electrode was 1.1309 cm^2 carried out in goldsmith.

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3. RESULTS AND DISCUSSION

3.1 XRD analysis

The XRD patterns of the BMT powders with various Mn contents were shown in Fig 1. The diffraction peaks were identified by using the standard powder diffraction data of BIT. The samples were scanned from 10° to 70° in 2θ with a step size of 0.01. It was found that all the powder consists of a single phase of bismuth – layered perovskite structure. The lattice parameters of BMT powders were slightly different from pure BIT. All the parameters were gradually decreased with respect compositions. So the volume of the crystals were reduced because of the Mn^{4+} ions were partially occupied by Ti^{4+} ions. This was due to the formation of oxygen vacancy may appear for charge compensation in the crystal. Lattice parameters and

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crystallite size of BMT powders were evaluated in Table 1.

Table 1. Lattice parameters of Mn doped BIT powders

Mn doped BIT powder	*a (Å)*	*b(Å)*	*c(Å)*	*FWHM of (117) plane (rad)*	*Crystallite size of (117)plane (Å)*
X=0.0	**5.4504**	**5.4281**	**32.6284**	**2.408E-3**	**649**
X=0.1	**5.4573**	**5.4168**	**32.9278**	**3.612E-3**	**432**
X=0.2	**5.3758**	**5.4049**	**32.6908**	**3.577E-3**	**437**
X=0.3	**5.4221**	**5.2951**	**32.7332**	**4.014E-3**	**392**
X=0.4	**5.4202**	**5.3406**	**32.3296**	**3.700E-3**	**425**

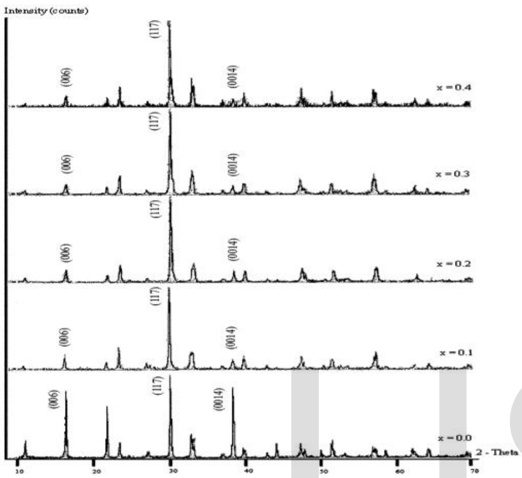

Fig. 1 The comparison of XRD spectrum of the Mn-doped $Bi_4Ti_3O_{12}$ powder

3.2 Dielectric Properties

The dielectric constant and the loss tangent of BMT ceramic samples were obtained by measuring the capacitance and dissipation factor with a LCR Digibridge meter (Quad Tech, 1730) operated at 1 kHz to 100 kHz and the comparison with the difference of two temperatures (room temperature & 50˚C), level 1.00 V and resistance auto-range. Dielectric constants, dielectric loss factors, loss current and AC conductivity for all compositions of BMT ceramic materials were illustrated in Fig (2 ~ 5). The dielectric and loss factor were increasing with dopant concentration but decreasing with frequencies. This was because manganese (Mn) had a lower electrical conductivity 0.006 x 10^6 $(\Omega cm)^{-1}$ than titanium (Ti) 0.219 x 10^6 $(\Omega cm)^{-1}$. Therefore, MnO_2 may become more dielectric than TiO_2 in BMT ceramic sample except composition (x = 0.1) which occurred lattice distortion among them. As dielectrics and dissipation factors increase, the imaginary parts of dielectrics or loss factors and dopant concentration of Manganese (Mn) rise. Besides, they happen to lose currents (I_L) and power dissipation become higher. The dielectric decreasing with applied alternating frequencies was that the relative capacitance was inversely proportional to frequency known as RC effect. But, the other fact of getting lower dielectric and higher loss current was that AC conductivity was rising with frequency and composition (x). The rising AC conductivity based on dissipation factor (tanδ) could be calculated by the equation;

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon_r \tan\delta$$

Although Manganese (Mn) has a lower conductivity than Titanium (Ti), the AC conductivity of BMT ceramic sample was increasing with dopant concentration of Manganese (Mn) as shown in Fig (5).Therefore, this fact needed to be considered by the p-n transitions of Manganese (Mn) and Titanium (Ti). The dielectric (ε_r) and dissipation factor (tanδ) were seriously depending on frequency, measuring applied alternating voltage level and temperature on the sample. The comparison of the dielectric, loss factor, loss current and AC conductivity between at room temperature and at 50°C with 10 kHz were shown in Fig (6 ~ 9) and their values were illustrated in Table 2 and Table 3.

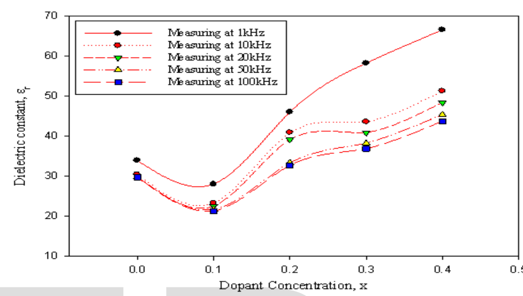

Fig. (2) Dielectric constant of BMT ceramic with the different dopant concentration at room temperature

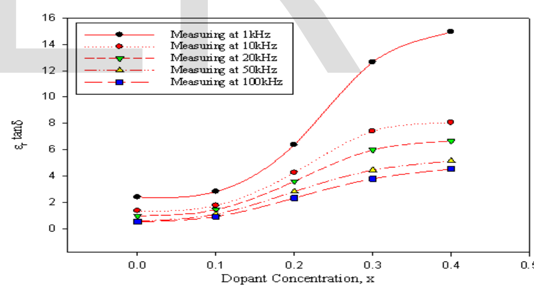

Fig. (3) Dielectric loss of BMT ceramic with the different dopant concentration at room temperature

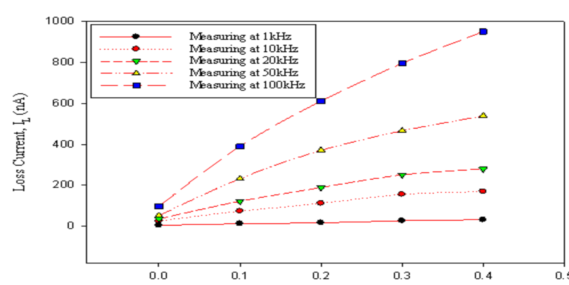

Fig. (4) Loss current of BMT ceramic with the different dopant concentration at room temperature

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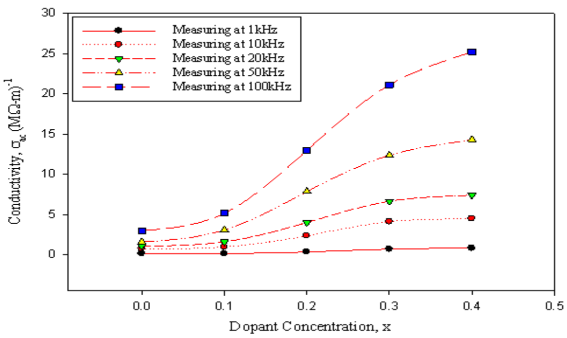

Fig. (5) AC conductivity of BMT ceramic with the different dopant concentration at room temperature

Table 2. Dielectric properties measuring at (Room Temperature, 10kHz) with respect to compositions

Composition	ε_r	$\varepsilon_r\ tan\delta$	$I_L\ (nA)$	$\sigma_{ac}(M\Omega m)^{-1}$
X=0.0	**30.446**	**1.364**	**24.518**	**0.759**
X=0.1	**23.310**	**1.758**	**73.730**	**0.978**
X=0.2	**40.961**	**4.260**	**111.671**	**2.370**
X=0.3	**43.623**	**7.407**	**155.338**	**4.121**
X=0.4	**51.323**	**8.058**	**168.981**	**4.487**

Table 3. Dielectric properties measuring at (50˚C, 10kHz) with respect to compositions

Composition	ε_r	$\varepsilon_r\ tan\delta$	$I_L\ (nA)$	$\sigma_{ac}(M\Omega m)^{-1}$
X=0.0	**8.898**	**0.634**	**39.860**	**0.352**
X=0.1	**16.738**	**0.797**	**50.128**	**0.443**
X=0.2	**21.200**	**1.522**	**79.805**	**0.847**
X=0.3	**26.126**	**4.345**	**136.672**	**2.417**
X=0.4	**26.716**	**4.510**	**153.363**	**2.509**

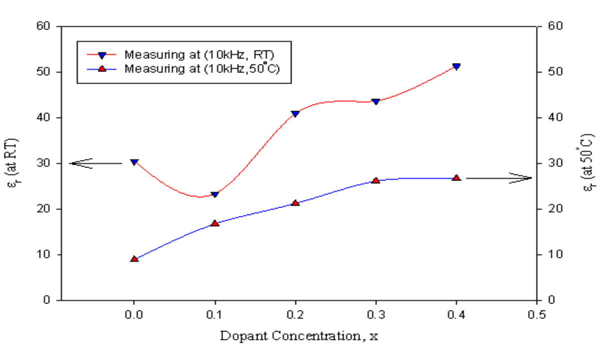

Fig. (6) The variation of dielectric constant measuring at two temperatures

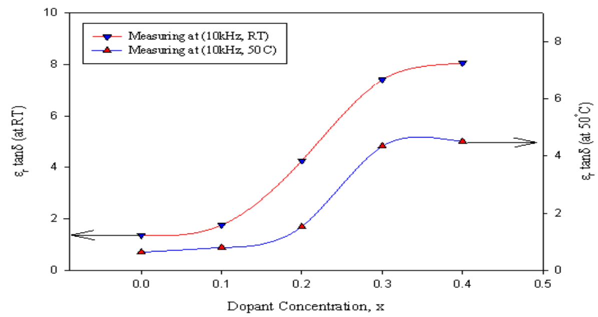

Fig. (7) The variation of dielectric loss measuring at two temperatures

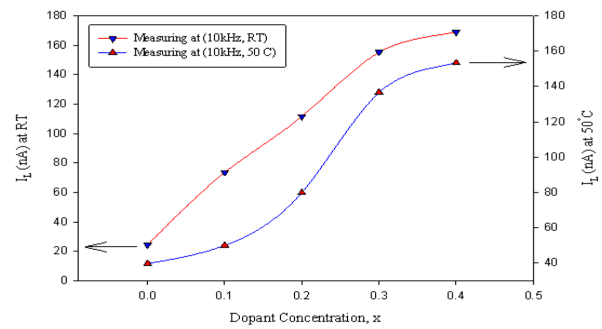

Fig. (8) The variation of loss current measuring at two temperatures

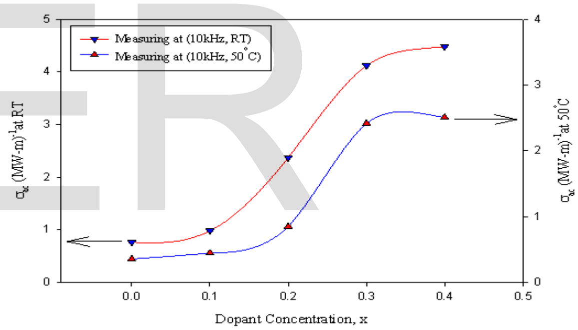

Fig. (9) The variation of AC conductivity measuring at two temperatures

3.3 P-E Hysteresis Measurement

To measure ferroelectric properties, the Cu-BMT-Cu ceramic was placed in the sample holder. A triangular derived voltage signal was applied to the basic Sawyar-Tower circuit. Applied frequency 10 kHz was a fined resonance situation for all samples. The value of remanent polarization P_r, spontaneous polarization P_s, and coercive field E_c could be counted in the screen of the oscilloscope. Fig (10) showed Ferroelectric hysteresis loop for different dopant concentration at room temperature at 10 kHz. As the result, ferroelectric hysteresis loops were changed with respect to stoichiometric compositions. From this figure, the good symmetrical polarizations of the samples were getting and the P_r, P_s value of BMT (x = 0.3) and (x = 0.4) were higher than others in the smaller value of electric field E_c. So, the values of P_r and P_s were going to be studied with different applied electric field. When the field was reduced below E_c, the loop shrinks, and it becomes a narrow

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ellipse beak with its major axis parallel to the almost horizontal portion of the fully developed loop.

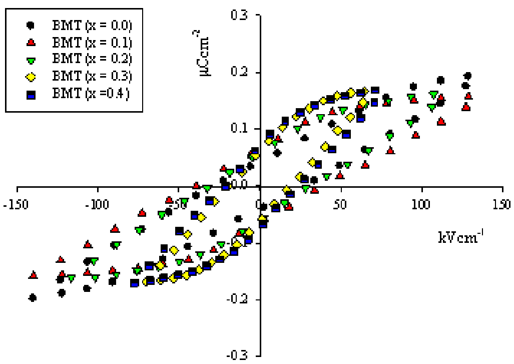

Fig. (10) Ferroelectric hysteresis loop for different dopant concentration at room temperature at 10 kHz

4. CONCLUSION

The preparation of Mn doped $Bi_4Ti_3O_{12}$ on electroceramics and the characterizations of the samples have been successfully investigated. The more manganese concentration in the composition of BMT, the more charge in dielectric and dielectric loss factors could be observed.During calculation of the loss current in the advance of measuring dielectric constant and dissipation factor, the fundamental logic and equation of R-C circuit must be considered as follow. When the applied frequency increases, dielectric constant ε_r and loss factor tanδ were decreased and loss current I_l was increased. When the applied temperature increased, all these three factors were decreased. Polarization properties of ferroelectric samples were assessed using P-E analysis. From the hysteresis loop measurement, BMT ceramic could be used as non-volatile ferroelectric random access memory applications.

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