Paper ID: MS-08

Improved Dielectric Properties of La/Mn Codoped Bismuth Titanate Ceramic

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Abstract

Undoped bismuth titanate, $Bi_4Ti_3O_{12}$ (BIT), La doped bismuth titanate, $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and La/Mn codoped bismuth titanate $Bi_{3.25}La_{0.75}Ti_{3-x}Mn_xO_{12}$ (BLTM) (x = 0.005, 0.01, 0.02) ceramic samples were prepared by solid state reactions. The influence of La/Mn cosubstitution in the crystal structure of BIT was investigated by XRD and IR spectroscopic studies. The XRD results show that all samples are polycrystalline and almost single phase with a bismuth-layered structure belonging to the crystalline phase of BIT. In IR spectra, three absorption peaks appeared at 814, 592 and 379 cm^{-1}, which were for the formation of titanate structure. In addition, two shoulders appeared at 313 and 470 cm^{-1} in support of the monoclinic symmetry of pure BIT. A new and relatively broad absorption peak appeared around 1015 cm^{-1} due to Mn doping in BLT corresponding to the stretching vibration of Mn-O bond. Dielectric measurements showed that the dielectric constant of the prepared samples decreased with increasing frequency and remained almost constant after 10 KHz. It was found that dielectric constant was increased and dielectric loss was reduced on La-doping. The effect of Mn codoping on the dielectric properties of BLTM was studied and it found that the optimum codoping concentration of Mn was 0.01 mol%.

Keywords: *Codoping, Solid-state reaction, Dielectric constant, Dielectric loss, XRD, IR.*

1. Introduction

Dielectric ceramic materials are useful in optical applications and device components such as filters, transmitters, reflectors, lenses and optical waveguides. They are also utilized widely in electronic devices such as capacitors, actuators, etc. These materials are usually characterized by their refractive indices, dielectric constants and dielectric losses. Dielectric materials with high values of refractive indices and dielectric constants but low dielectric losses can markedly reduce the size of devices, which is highly desirable in integrated circuits, optical systems, electronic systems, and electro-optical systems [1].

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) is a well-known member of the Aurivillius family of bismuth-based ferroelectric compounds with a layered structure $(Bi_2O_2)^{2+}(Bi_2Ti_3O_{10})^{2-}$ [2]. BIT has attracted more and more attention recently because it is considered to be a potential candidate for lead-free dielectric and ferroelectric ceramics [3]. BIT ceramics have been used in multilayer ceramic capacitors, ultrasonic generators, actuators, ferroelectric random access memory, and so on as it has strong anisotropic character, low dielectric dissipation factor, high dielectric breakdown strength, low aging rate and electro-optic switching behavior, high temperature coefficient of resonant frequency [4-6]. Although BIT is considered to be a potential candidate for lead-free chemical composition, high $2P_r$, and other good electrical properties, it suffers from a strong fatigue failure after 10^{12} cycles and high processing temperature [7]. Recently, it has been reported that A-site modification in BIT by Lanthanides (La, Pr, Sm and Nd) improves fatigue behavior significantly [8]. Among them, the La doped BIT, namely $Bi_{3.25}La_{0.75}Ti_3O_{12}$, ceramic is fatigue free under repeating switching cycle but in this case the $2P_r$ is decreased largely from 50 μC/cm^2 to 30 μC/cm^2 while the coercive field ($2E_c$, 100 KV cm^{-1}) is reasonable [7]. In this investigation, Mn ion is chosen for the B-site modification of La doped BIT because Mn ion shows a peculiar behavior for its variable valencies. In the present work, pure BIT, La doped BIT and La/Mn codoped BIT ceramics have been prepared by the conventional solid-state reaction method. The phase assemblages and dielectric properties of the ceramic samples have been investigated and compared with those of BIT.

2. Sample Preparation and Experimental Setup

Pure BIT, La-doped BIT and La/Mn codoped BIT samples have been prepared by solid-state reaction. A reagent grade Bi_2O_3 (Merck, Germany), La_2O_3 (Wako Pure Chemical Industries Ltd., Japan), TiO_2 (Merck, India) and MnO_2 (Wako Pure Chemical Industries Ltd., Japan) powders have been used as the starting materials. Sample preparation has been completed by the following steps:

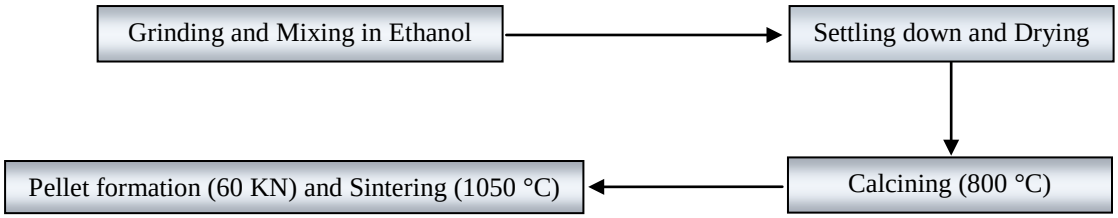

Fig. 1. Different steps of sample preparation

Stoichiometric amounts of starting materials were weighed out, mixed and milled in ethanol for 24 h in a ball mill. After ball milling, the mixture was kept in a beaker for 24 h to settle down the mixed powder. The ethanol was decanted out and the slurry was put into an oven for drying. The dried powder was again grounded in a mortar and calcined at 800 °C for 4 h. The rate of temperature raising and cooling was maintained at 10 °C/min. The calcined powders were mixed with 2.5% PVA solution in a mortar and then pressed at 60 KN to form pellet. The prepared pellets were then sintered at 1050 °C for 1 h. After sintering the color of $Bi_4Ti_3O_{12}$, $Bi_{3.25}La_{0.75}Ti_3O_{12}$, $Bi_{3.25}La_{0.75}Ti_{2.995}Mn_{0.005}O_{12}$, $Bi_{3.25}La_{0.75}Ti_{2.99}Mn_{0.01}O_{12}$ and $Bi_{3.25}La_{0.75}Ti_{2.98}Mn_{0.02}O_{12}$ samples were white shadow, white shadow, brown shadow, light brown and brown respectively.
A natural convection oven (JSR, JSON-100), a Carbolite furnace (ELF 11/6B) and a Shimadzu hand pressure gauge machine were used for drying, calcining and sintering, and making pellet. The XRDs were taken by an X-ray diffractometer (X'Pert-PRO, Philips, Japan). For measurements of frequency dependent capacitance, impedance and dielectric constant, a Precision Impedance Analyzer (model 4294A, range 40 Hz to 110 MHz, Agilent Technologies, Japan) was used. The frequency dependent capacitance was taken in the frequency range (1 KHz to 1 MHz) for all samples. A FTIR spectrophotometer (Spectrum 100, Perkin Elmer, resolution =1 cm^{-1}) was used to take spectra within 2000 – 300 cm^{-1}.

3. Results and Discussion

The experimental results on characterization and dielectric properties measurements of the samples are given and discussed below:

Structural Study

The structures and phases of the sintered BIT, BLT and BLTM samples were characterized by X-ray diffraction patterns (X-ray diffractometer, X'Pert-Pro, Philips, Japan using Cu *Kα* (λ = 1.5405Å) radiation). The XRD patterns of the ceramic samples are shown in Fig. 2. All the peaks are indexed according to the reference code 36-1486, which indicates that the obtained BIT ceramic is polycrystalline in nature and it contains single phase of bismuth-layered perovskite structure with preferred (117) and (00*l*) orientations [7]. However, in the XRD patterns there are three unknown peaks observed at (27.9198°), (28.7277°) and (49.3098°). These peaks indicate that a trace amount of another phase is present in the sample. This phase could be pyrochlore ($Bi_2Ti_2O_7$) phase [9]. In addition, the slim width of the diffraction peaks indicates the large crystallite size of the ceramic [10].
Fig. 3 shows the FTIR spectra of the calcined powders within 2000 – 300 cm^{-1}. From the spectra of BIT, it is found that two sharp absorption peaks appear at 814 and 592 cm^{-1} which correspond to stretching vibrations of Bi-O and Ti-O bonds, respectively [11]. Another sharp absorption peak appears at 379 cm^{-1} that is related to the bending vibration of Ti-O bond [12]. In addition, two shoulders are observed at 470 and 313 cm^{-1}. The absorption peaks at 814, 592 and 379 cm^{-1} is a characteristics feature of the formation of titanate structure [13]. It is found that the IR spectra of BLT powder were similar to those of BIT powder, except small shifts of the absorption peaks with reduction of the intensities. The adsorption peaks at 592 cm^{-1} and 379 cm^{-1} were shifted to 607 cm^{-1} and 392 cm^{-1}, respectively, in FTIR spectra of BLT, while the intensity of the band at 814 cm^{-1} is significantly decreased [12]. It is also found that shoulders at 470 and 313 cm^{-1} in BIT are disappeared on La

doping (at 0.75). It is well known that crystal structure of pure BIT is monoclinic [15]. The monoclinic phase undergoes a structural phase transition to orthorhombic due to La doping at 0.66 doping level [14]. Therefore, the disappearance of shoulders at 470 and 313 cm^{-1} could be related to the monoclinic to orthorhombic phase transition.

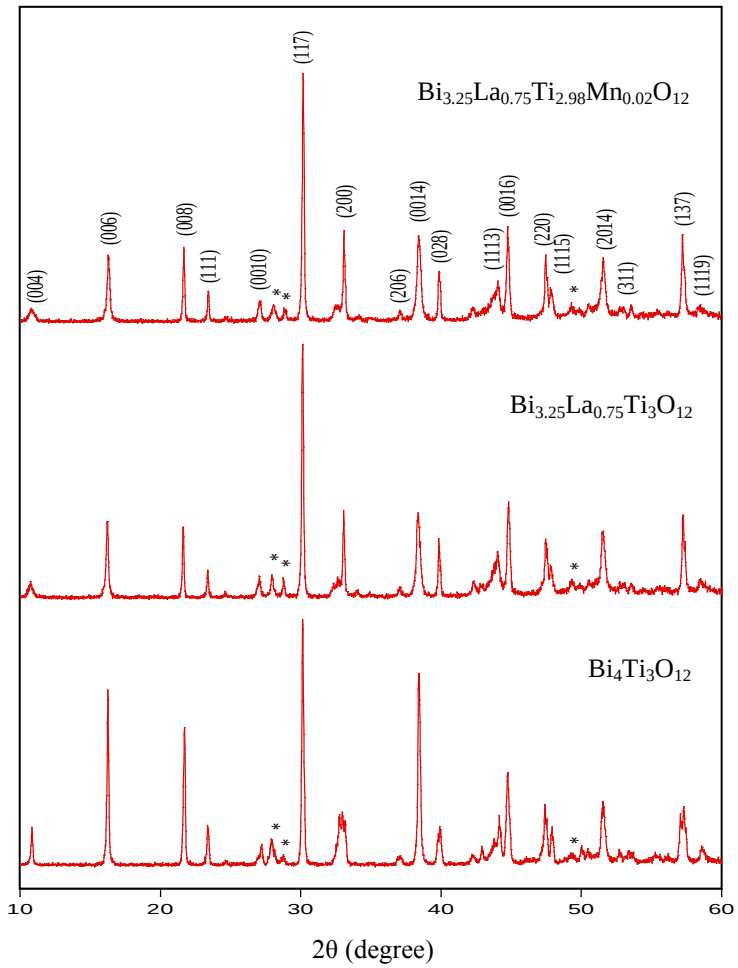

Fig. 2. X-ray diffraction patterns of BIT ceramic samples sintered at 1050 ºC for 1 hour (∗Pyrochlore phase)

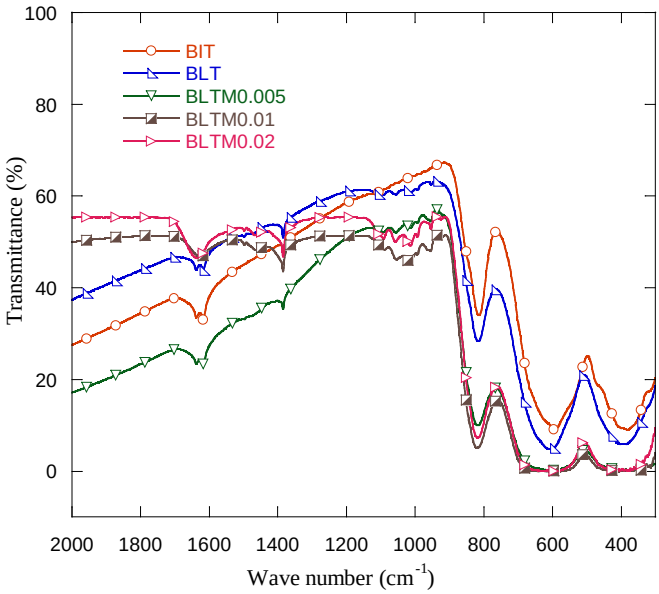

Fig. 3. Combined FTIR spectra of BIT, BLT and BLTM (x = 0.005, 0.01, 0.02) powder calcined at 800 ºC for 4 hours

From figure it is noticed that with increasing doping level of Mn in BLT, a dramatic change in FTIR spectra is observed. The absorption peaks at 607 cm^{-1} and 392 cm^{-1} become defused. Moreover, a new and relatively broad absorption peak appears at ~1015 cm^{-1}, which may related to the stretching vibration of Mn-O bond [15]. Therefore, it is reasonable to speculate that the new absorption peak resulting from the Mn-O vibrational mode could be due to the replacement of Ti by Mn in the TiO_6 octahedron [16]. The intensity of this peak gradually increases with the increase of Mn doping level. The gradual enhancement of the new absorption peak with the increase of Mn doping level further confirms the Mn substitution at the *B* site in BLTM ceramic samples [16].

Study of Dielectric Properties

Fig. 4 shows the variation of dielectric constant with frequency at room temperature for BIT, BLT and BLTM samples. It is seem that the dielectric constant of the sample is relatively high at lower frequency region in comparison to that in higher frequency region and the value becomes constant after 10 KHz for all samples. The dielectric constant of La doped BIT is higher than that of pure BIT. The increment of dielectric constant due to La doping can be explained as follows: It is known that defects such as Bi vacancies accompanied by oxygen vacancies degrade the dielectric properties in BIT [17]. These vacancies arise during sintering process due to the high volatility of Bi ions [18]. La doping improves the dielectric properties of bismuth titanate as it suppresses the volatility of Bi during sintering and reduces the oxygen vacancies in the ceramics [19]. It is also found that the dielectric constant of Mn doped BLT is increased with the increase of Mn doping level to a certain content (up to x = 0.01) and then decreased with the increase of Mn doping level. The increment of dielectric constant can be explained as follows: Mn doping at a suitable level improved the dielectric properties of the BLT samples by producing extrinsic oxygen vacancies that reduced the number of intrinsic bismuth vacancies [20]. The optimum Mn doping level in BLT towards the better dielectric performance is 0.01 mol%.
In addition the ionic radius of Mn^{4+} (0.060 nm) is a little smaller than that of Ti^{4+} (0.068 nm). When host Ti ions are replaced by small substitutional Mn ions, these ions may be located in the off-centered positions, which enhances the ionic dispalcement or distortion of TiO_6 octahedron, thus improving the dielectric property [16]. Excessive Mn doping reduced the dielectric properties of BLT ceramic. This can be explained by the ways: when Mn content is higher in BLT, ion-doped crystal lattice have not entered the interior in the grain, it gather in the grain boundary which impede the motion of the domain wall in the electric field. The domain wall motion has an important role to dielectric properties. By impeding domain wall motion excessive Mn doping reduced the dielectric constant [21].

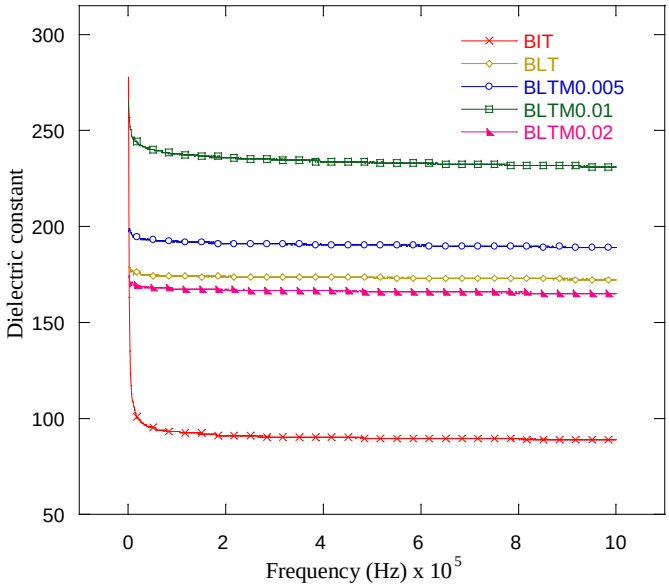

Fig. 4. Dielectric constant of BIT, BLT and BLTM (x = 0.005, 0.01, 0.02) samples as a function of frequency

Fig. 5 shows the dielectric losses of BIT, BLT and BLTM samples. It is seen that the loss tangents of BLT and BLTM ceramics are lower than that of pure BIT. This reduction of loss tangent could be due to the reduction of free charge, like oxygen vacancy, bismuth vacancy, etc.

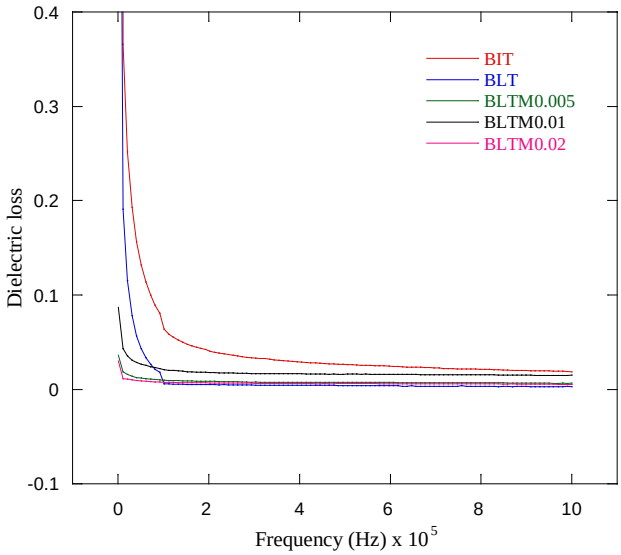

Fig. 5. Dielectric loss of BIT, BLT and BLTM samples as a function of frequency

4. Conclusions

BIT, La doped BIT and La/Mn codoped BIT ceramic samples fabricated by the solid-state reaction method exhibit polycrystallinity and almost single phase of bismuth-layered structure belonging to the crystalline phase $Bi_4Ti_3O_{12}$. The appearance of three absorption peaks at 814, 592 and 379 cm^{-1} in IR spectra of the prepared samples confirms the formation of titanate structure. Dielectric constant of the prepared samples decreases with the increase of applied frequency and then remains more or less constant after 10 KHz. The incorporation of La

in BIT suppressed the volatilization of Bi^{3+} during sintering and reduces the oxygen vacancies in the sintered sample. As a result, the dielectric constant increases and the dielectric loss are significantly reduced with La doping. The dielectric constant of Mn doped BLT increases with increasing Mn doping up to x = 0.01 and then decreases due to the domain wall pinning. From these results it is observed that BLTM sample shows the best dielectric properties for the Mn doping level at 0.01 mol%.

Acknowledgements

Authors are grateful to the Central Science Laboratory, University of Rajshahi, Rajshahi-6205, Bangladesh and also to the Materials Science Division, Atomic Energy Center, Dhaka, Bangladesh for providing laboratory facilities. They give thanks to the Ministry of Science and Information & Communication Technology (MOSICT) of Peoples Republic of Bangladesh for financial support to this research.

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