

Research Article

Effect of Processing on Synthesis and Dielectric Behavior of Bismuth Sodium Titanate Ceramics

Vijayeta Pal,¹ R. K. Dwivedi,¹ and O. P. Thakur²

¹Department of Physics and Material Science & Engineering, Jaypee Institute of Information Technology, Noida 201307, India

²Electroceramics Group, Solid State Physics Laboratory, Defence Research and Development Organization (DRDO), Timarpur, Delhi 110054, India

Correspondence should be addressed to Vijayeta Pal; vijayetapal@yahoo.in

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An effort has been made to synthesize polycrystalline $(\text{Bi}_{1-x}\text{La}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (abbreviated as BLNT) system with compositions $x = 0, 0.02, \text{ and } 0.04$ by novel semiwet technique. Preparation of A-site oxides of BLNT for composition $x = 0$ was optimized using two precursor solutions such as ethylene glycol and citric acid. The XRD patterns revealed that the sample prepared by ethylene glycol precursor solution has single phase perovskite structure with a rhombohedral symmetry at RT as compared to the sample prepared by citric acid. Ethylene glycol precursor has been found to play a significant role in the crystallization, phase transitions, and electrical properties. The studies on structure, phase transitions, and dielectric properties for all the samples have been carried out over the temperature range from RT to 450°C at 100 kHz frequency. It has been observed that two phase transitions (i) ferroelectric to antiferroelectric and (ii) antiferroelectric to paraelectric occur in all the samples. All samples exhibit a modified Curie-Weiss law above T_c . A linear fitting of the modified Curie-Weiss law to the experimental data shows diffuse-type transition. The dielectric as well as ferroelectric properties of BLNT ceramics have been found to be improved with the substitution of La elements.

1. Introduction

Lead oxide-based ceramics with perovskite structure have been the subject of attraction for high-performance sensors, actuators, transducers, and other applications, owing to their superior dielectric, piezoelectric, and electromechanical coupling coefficients. Applications are restricted to temperature range -50 to 150°C [1]. However, in recent years many fields have expressed the need for actuation and sensing which can be used at higher temperatures ($>400^\circ\text{C}$) such as automotive, aerospace, and related industrial applications. On the other hand, in most of the cases lead constitutes more than 60% of the composition of these piezoelectric devices. Lead, known to be highly toxic and volatile, is released to the atmosphere during sintering causing serious environmental and health problems. Another cause for concern is the disposal of these products at the end of the life cycle. Considering all these health concerns posed by lead, multinational governments

like the European Union have enacted laws that ban the use of lead in the manufacture of many industrial products [2]. This has led to the replacement of lead (Pb) in the field of piezoelectric ceramics. A lot of research has been carried out on lead-free piezoceramic products in the last fifty years but in the last few years, the momentum has tremendously increased, accounting for about 75% of all published works in this field. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - (BNT-) and $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ - (KNN-) based materials are two main material systems with perovskite structure, which have been studied to find the substitute of PZT for lead free piezoelectric applications. Pure BNT was discovered by Smolenskii et al. [3] and is a ferroelectric having Bi^{3+} and Na^+ complexes on the A-site of ABO_3 -type perovskite structure with a rhombohedral symmetry. Because of a large remanent polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) at room temperature, BNT ceramic is considered as one of the promising candidates for lead free piezoelectric ceramics [4]. However, the poling of pure BNT ceramic is

very difficult due to its high coercive field ($E_c = 73$ kV/cm). So, the pure BNT ceramic usually exhibits weak piezoelectric properties. Therefore, a number of BNT-based ceramics were prepared to improve the electrical properties of this material by the convectional solid state method [5, 6]. Recently, a lot of efforts have been made to prepare the material by various chemical methods, such as hydrothermal process [7], citrate method [8, 9], sol-gel, autocombustion [10], and stearic acid gel route [11]. In the present work, A-site oxides of lead-free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramics were optimized using two precursor solutions such as ethylene glycol and citric acid at low calcination temperature (750°C) and further some La doped BNTs (BLNTs) have been developed using ethylene glycols precursors by a novel semiwet technique and structural, dielectric, and ferroelectric properties have been studied for both systems. To the best of our knowledge, BLNT system has been synthesized for the first time using semiwet technique. This technique has been applied to make other systems enhance its properties [12].

2. Experimental Procedures

A novel semiwet technique was used to prepare lead-free ceramic $(\text{Bi}_{1-x}\text{La}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BLNT) system. These compositions were prepared using analytical-grade metal oxides or nitrate powders of sigma Aldrich as raw materials such as Bi_2O_3 (99%), La_2O_3 (99%), NaNNO_3 (99%), TiO_2 (99.9%) citric acid, and ethylene glycol. In this method, A-site of BLNT with composition $x = 0$ was prepared by using two different precursor solutions; the first one is citric acid, and; the second is ethylene glycol. In the first process, an appropriate amount of citric acid solution was added to the solution of nitrates of A-site cations in a beaker (C/M $\sim 1:1$). Aqueous ammonia in the solution form was added drop by drop to adjust the pH value of the solution in the range of 6–8. The precursor solution was dehydrated by putting on heater with continuous stirring at 80°C for 3 hrs to form a viscous gel which was placed in an oven at 150°C for overnight to combust the gel into ash powder. In the second process, stoichiometry amount of the solution of nitrates of A-site cation was dissolved with the ethylene glycol (E/M $\sim 1:1$) with continuous stirring for 30 min to get homogeneously mixed solution. The precursor solution was dehydrated by the same conditions, which is discussed in the first method to form a gel into ash powder. Both precursor solutions are expected to distribute the cations atomically homogeneously throughout the polymeric structure forming a stable polymeric complex, which was combusted at appropriate temperature ($T \sim 500^\circ\text{C}$) in the form of ash powder. The ash, highly fine, homogeneous, and highly reactive powder was mixed with appropriate amounts of TiO_2 powder thoroughly in ethanol using mortar pestle for 2 hrs followed by solid state route. These powders were dried and calcined at 750°C (2 hrs) for BNT-CA and BNT-EG and calcined at 850°C (2 hrs) for BLNT samples. The calcined powder was mixed thoroughly with a polyvinyl alcohol (PVA) binder solution and then pressed into the form of disk with 10 mm diameter. All samples are in pellet form, kept in alumina boat, and

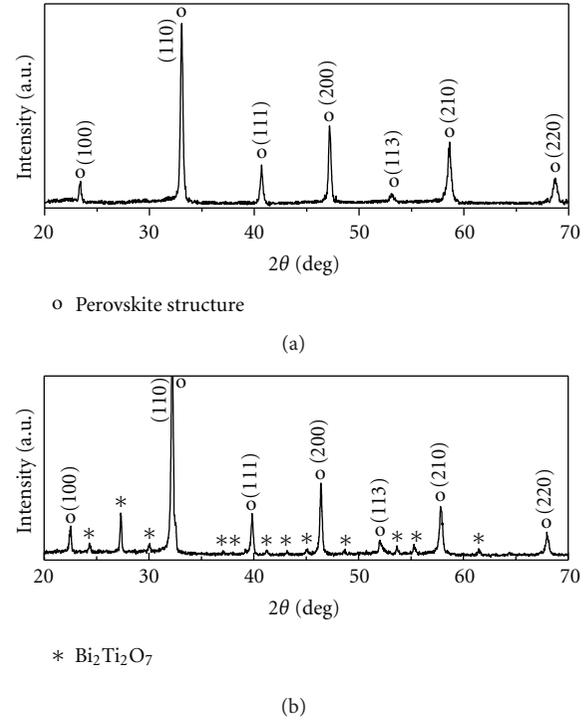


FIGURE 1: XRD patterns of (a) BNT-EG and (b) BNT-CA samples.

sintered at temperature 1150°C for 2 hours. Two pellets of each composition were electroded with silver paint on both the surfaces of the samples for the subsequent electrical measurements. The crystallite size of all the samples in BLNT system was calculated using Debye-Scherrer formula ($D = 0.89\lambda/\beta \cos \theta_B$) where D is the average crystallite size, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM), and θ_B the diffraction angle. The corresponding values are reported in Table 1.

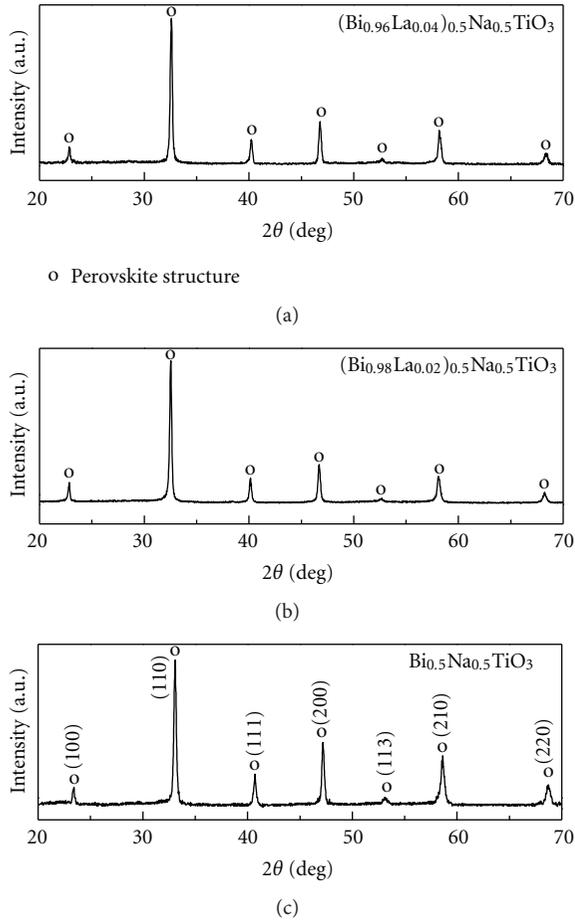
The crystalline structure of the sintered samples was examined using X-ray diffraction (XRD) analysis with $\text{Cu-K}\alpha$ radiation (DX-1000). The surface morphology of sintered ceramics was observed by scanning electron microscopy (SEM, model JEOL A 800). The dielectric constant ϵ_r and dielectric loss ($\tan \delta$) of the ceramic samples at 100 kHz were measured as a function of temperature over the temperature range from room temperature to 450°C using an LCR meter (Hioki 3522). A conventional P - E loop tracer (Marine India), which is based on Sawyer-Tower circuit, was used to measure the polarization-electrical field (P - E) hysteresis loop at 50 Hz.

3. Results and Discussion

In the present work, preparation of pure $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ was optimized using two chemical precursors, citric acid and ethylene glycol. These samples are abbreviated as BNT-CA and BNT-EG (Figures 1(a) and 1(b)). It is observed from the XRD patterns that the sample prepared by ethylene glycol precursor solution has shown better phase formation, whereas BNT-CA has formed partially along with

TABLE 1: Dielectric properties of all BLNT system, prepared using ethylene glycol precursor.

Composition (x)	Lattice parameter $a = b = c$ (Å)	Volume (m^3)	ϵ_r at RT	Tan δ at RT	ϵ_r at T_m	Tan δ at T_m	T_d °C	T_m °C	γ	D (nm)
BNT ($x = 0$)	3.868	$5.78 * 10^{-29}$	705	0.040	3200	0.08	180	353	1.26	34.98
BLNT ($x = 0.02$)	3.931	$6.07 * 10^{-29}$	1036	0.044	3630	0.03	200	355	1.49	39.33
BLNT ($x = 0.04$)	3.922	$6.03 * 10^{-29}$	3020	0.045	5630	0.05	210	380	1.80	34.81

FIGURE 2: XRD patterns of BLNT system with compositions $x = 0, 0.02, \text{ and } 0.04$.

the presence of other phase identified as $\text{Bi}_2\text{Ti}_2\text{O}_7$ [13]. The experimental density observed in BNT-EG sample was 5.77 gm/cm^2 which is 95% of theoretical density and the experimental density observed in BNT-CA sample was 5.56 gm/cm^2 which is 91% of theoretical density. Therefore, a typical $(\text{Bi}_{1-x}\text{La}_x)_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BLNT) system with compositions $x = 0.02$ and 0.04 was prepared by semiwet technique using ethylene glycol precursor, calcined at 850°C . The XRD patterns of all the samples in BLNT system have shown single phase formation with a rhombohedral symmetry in Figure 2.

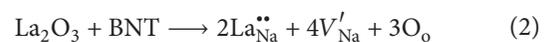
Pure BNT and BLNT powders have rhombohedral symmetry at room temperature. However, rhombohedral structure is hard to distinguish due to the overlapping of peaks that

could be due to nearly cubic lattice parameter. Owing to small degree of rhombohedral distortion, diffraction lines were indexed on the basis of pseudocubic unit cell [14] and lattice parameters of all the BLNT samples, prepared by ethylene glycol, are calculated by using the Unit Cell program package [15]. There is a variation in the lattice parameters because of the different sizes of ionic radius of La^{3+} (1.03 \AA) which are close to Bi^{3+} ionic radius (0.96 \AA) and Na^+ (0.99 \AA). The values in the parentheses refer to the Shannon's effective ionic radius with the coordination number of six taken from [16].

The microstructure of the pure BNT ceramics, prepared by semiwet using ethylene glycol and citric acid, sintered at 1150°C is shown in Figure 3. Ethylene glycol precursor plays a significant role in the grain growth and densification. The microstructure of pure BNT-EG ceramics is denser, homogeneous, and uniform grains with grain size of $2.12 \mu\text{m}$ as compared to BNT-CA with grain size of $1.19 \mu\text{m}$.

The dielectric measurements of electroded samples of BNT-EG, BNT-CA, and BLNT samples were carried at 100 kHz frequency over temperature range from room temperature to 450°C and are shown in Figures 4(a), 4(b), 4(c), and 4(d), respectively.

Two dielectric anomalies in all the samples are shown at temperatures T_1 and T_2 , termed as " T_d " and " T_m " respectively, which corresponds to dielectric transitions from ferroelectric (FE) to anti-ferroelectric (AFE) and anti-ferroelectric (AFE) to paraelectric (PE), respectively. The corresponding peaks also appear in $\tan \delta$ versus T plots. However, the low value of dielectric constant of the sample, prepared using citric acid (BNT-CA), may be due to formation of other phases of $\text{Bi}_2\text{Ti}_2\text{O}_7$, which hampers the one dielectric anomaly and relative value of dielectric constant in this sample. It has been observed that the T_d and T_m shift to higher temperature with increasing the concentration of La^{3+} . The partial replacement of A-site cation, with larger ionic radius cations and larger amount, decreases the relative displacement of B-site cation with respect to the oxygen octahedral cage and hence the increase in transition temperature is observed with substitution of La at A-site. It is obvious that La^{3+} (1.03 \AA) can occupy the A-site of Bi^{3+} (0.96 \AA) or Na^+ (0.99 \AA). When La^{3+} occupies A-site of Na^+ , it will lead to charge imbalance, which creates defects on A-site. In general, A-site (Bi^{3+} and Na^+) substitution by La^{3+} in BNT ceramics can be formulated in the following way:



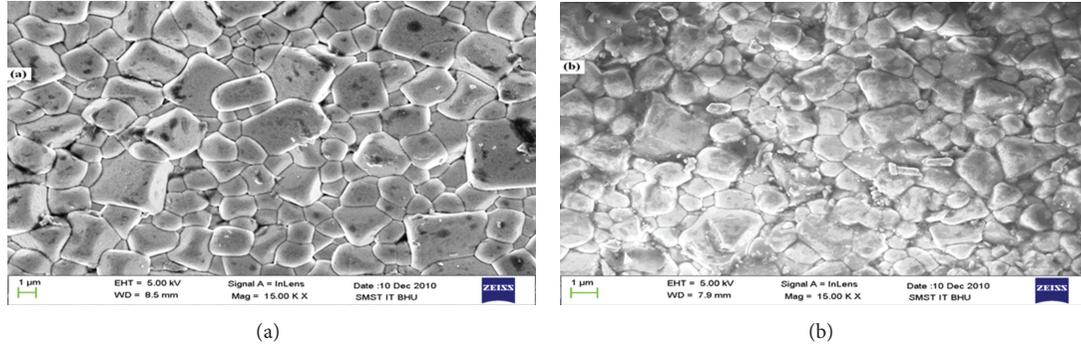


FIGURE 3: Microphotographs patterns of (a) BNT-EG and (b) BNT-CA samples.

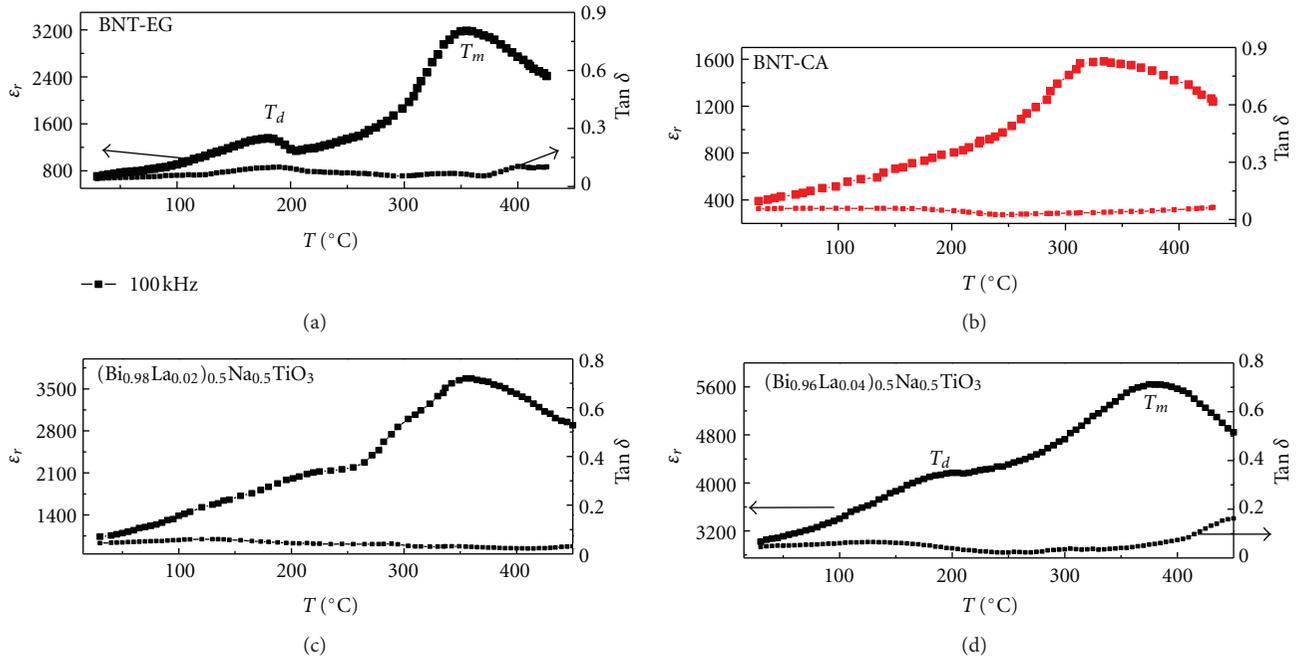


FIGURE 4: Variations of ϵ_r and $\tan \delta$ with temperature for samples (a) BNT-EG, (b) BNT-CA, (c) BLNT with $x = 0.02$, and (d) $x = 0.04$.

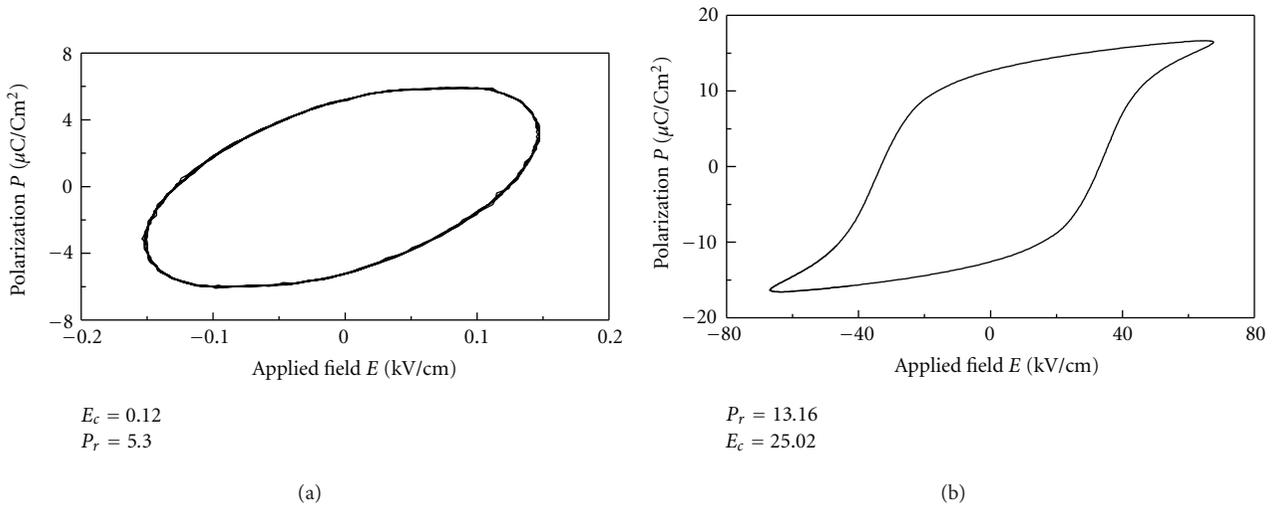


FIGURE 5: The P - E hysteresis loops at RT (50 Hz) (a) for BNT-CA and (b) BNT-EG.

TABLE 2: Ferroelectric properties of all saturated BLNT system, prepared using ethylene glycol precursor.

Composition (x)	P_r ($\mu\text{C}/\text{cm}^2$)	P_{max} ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
BNT-EG ($x = 0$)	13.16	16.90	25.02
BLNT ($x = 0.02$)	13.33	17.86	24.96
BLNT ($x = 0.04$)	17.70	20.60	36.73

When La^{3+} occupies Bi-site, as shown in (1), the substitution of Bi^{3+} by La^{3+} may cause the slack of BLNT lattice. The lattice deformation can make the ferroelectric domains reorientation more easily. It leads to the enhancement of dielectric as well as ferroelectric properties. Additionally, La^{3+} can also occupy the A-site of Na^+ , as shown in (2). In this case, the valence of La^{3+} ion is higher than that of Na^+ ion. To maintain overall electrical neutrality, La^{3+} acts as a donor leading to some Na-site vacancies [V'_{Na}], which can relax the strain caused by reorientation of domains. Therefore, the movement of the domains becomes easier and thus the electrical properties of the BLNT ceramics are improved significantly. Thus, the substitution of La^{3+} in BNT system has significantly influenced the phase transition and dielectric behavior (Figures 4(c) and 4(d)). The highest value of ϵ_r (~ 3020) and lowest value of $\text{Tan } \delta$ (~ 0.045) are obtained with the composition $x = 0.04$ in the BLNT system at room temperature. The physical and dielectric properties of all the BLNT samples are tabulated at RT (100 kHz) in Table 1.

It shows the typical character of a ferroelectric behavior around transition temperature because of diffused phase transition. Dielectric constant exhibits strong frequency dependence above T_d and the maximum value of ϵ_r decreases as frequency increases in the BNT-EG samples suggesting that the ceramic is relaxor ferroelectric. The diffuseness in the phase transition can be described by $1/\epsilon_r - 1/\epsilon_{r\text{max}} = C^{-\gamma}(T - T_m)^\gamma$ in relaxor ferroelectrics [17], where $\epsilon_{r\text{max}}$ is the maximum value of dielectric constant at T_m , γ is the degree of diffuseness, and C is the curie-like coefficient. γ can have a value ranging from 1 for normal ferroelectric to 2 for an ideal relaxor ferroelectric. This sample exhibits a linear relationship. The value of the exponent " γ " was determined by least-squared fitting experimental data to the equation which is in the range of 1.50 to 1.80. This confirms the diffuse phase transition in BLNT-EG system. The polarization-electrical field (P - E) hysteresis loop is shown in Figures 5(a) and 5(b). It has been found that the P - E loop of BNT using citric acid is round shaped, not well developed (saturated), Figure 4(a). BNT-CA sample gets breakdown with increasing electric field. This may be due to (I) large leakage current and (II) due to insufficient annealing process. P - E loop for BNT sample prepared using ethylene glycol is well developed or saturated, Figure 5(b).

This may be attributed to smaller grain size and relatively better density of the samples and confirm that all the samples are ferroelectric in nature.

The ferroelectric properties of all the BLNT system are tabulated at RT (50 Hz) in Table 2.

4. Conclusion

In summary, ethylene glycol prepared samples have revealed better crystallization of pure phase for BNT-EG sample. XRD patterns have revealed that the sample BNT-EG has single phase perovskite structure with a rhombohedral symmetry at RT. The structural, phase transition, and electrical properties of all the samples were investigated. The Bismuth sodium titanate, prepared by ethylene glycol precursor, has not only shown excellent dielectric but also ferroelectric behavior. The BNT sample has high value of dielectric constant ($\epsilon_r = 705$), dielectric loss ($\text{Tan } \delta = 0.04$), remnant polarization ($P_r = 13.16 \mu\text{C}/\text{cm}^2$), and Coercive field ($E_c = 25.06 \text{ kV}/\text{cm}$) at room temperature. The relatively highest value of dielectric constant for BLNT with composition $x = 0.04$ may be attributed to the La doping. Composition with La substitution of $x = 0.04$ has shown the highest value of dielectric (3020) constant and low loss (0.045) as well as the highest value of remanent polarization ($P_r = 17.70 \mu\text{C}/\text{cm}^2$). The transition temperature T_m is also maximum (385°C) for this composition which reveals that the material can be useful for high-temperature device applications.

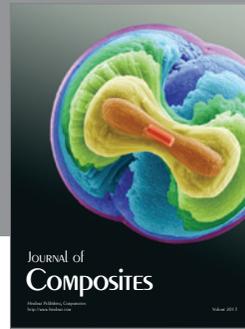
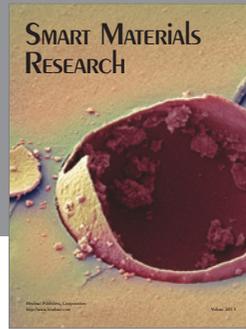
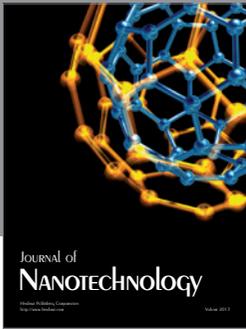
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