Chapter-5

Investigation of Oxide Ion Migration in Bi-Deficient Mg^{2+} Doped Sodium Bismuth Titanate

CHAPTER 5: Investigation of Oxide Ion Migration in Bi-deficient Mg^{2+} Doped Sodium Bismuth Titanate

5.1 Introduction

Ion dynamics and the degradation mechanism of NBT has been discussed in chapter 3 and 4. Also, it has been reported that the synthesis of the stoichiometric NBT is challenging because of the volatile nature of sodium and bismuth. Experimental and theoretical investigation suggest that the processing conditions can alter the physical properties of any material [183]. Although, NBT and accepter doped Bi deficient NBT compositions are mostly synthesized by solid-state reaction routes. A very few reports of synthesis of NBT based compositions are found via solution-based techniques. Reshetnikova et al. have synthesized the NBT based ferroelectric compositions employing the hydrothermal method with sodium hydroxide solution and studied its phase formation behaviour [184]. Synthesis of Sodium and Potassium Bismuth Titanates (NBT/KBT) via hydrothermal method is also reported by the M. M. Lencka et al. and they considered the yield diagrams and stability of the studied systems and also optimised the processing parameters for investigated KBT and NBT systems [185]. Kim et al. have synthesized the Bismuth Sodium Titanate nano-powders by sol-gel method and studied the structural parameters of the compositions [145]. A few more reports of solution-based synthesis of NBT derived compositions were also found, but these reports generally explored the structural and processing parameters of the investigated systems [144][146][183] [186]–[190].

In this chapter, the influence of the polyol mediated synthesis on the structural and electrical properties of Bi-deficient NBT samples has been studied. In polyol mediated synthesis, ethylene glycol molecules (EG) acts as a capping agent in addition to reaction media. Therefore, we can get fine particles with homogeneous phase, narrow particle distribution and better surface area at relatively lower temperatures. The effects of partial substitution of Mg^{2+} on the Ti^{4+} site with oxygen migration in correlation with structural distortions and electrical conductivity has been systematically discussed for all the investigated compositions. The effects of partial substitution of Mg^{2+} on the Ti^{4+} site with oxygen migration in correlation with structural distortions and electrical conductivity has been systematically discussed. Here onwards, $Na_{0.5}Bi_{0.49}TiO_3$, $Na_{0.5}Bi_{0.49}Ti_{0.99}Mg_{0.01}O_3$, $Na_{0.5}Bi_{0.49}Ti_{0.98}Mg_{0.02}O_3$, $Na_{0.5}Bi_{0.49}Ti_{0.97}Mg_{0.03}O_3$ oxides areabbreviated as NBT4900, NBT4901, NBT4902 and NBT4903, respectively.

5.2 Experimental Procedure

$Na_{0.5}Bi_{0.49}TiO_3$, $Na_{0.5}Bi_{0.49}Ti_{0.99}Mg_{0.01}O_3$, $Na_{0.5}Bi_{0.49}Ti_{0.98}Mg_{0.02}O_3$, and $Na_{0.5}Bi_{0.49}Ti_{0.97}Mg_{0.03}O_3$ systems were prepared via polyol mediated synthesis. High purity grade reactants of Na_2CO_3 (99.8%, Alfa Aesar), Bi_2O_3 (99.9%, SRL), Titanium Isopropoxide ($C_{12}H_{28}O_4Ti$) (99.95%, Alfa Aesar), MgO (99.9%, Alfa Aesar) were used as the precursors. The details of the experimental procedures have been described in chapter 2.

The phase of annealed powder were analyzed by X-ray diffraction (XRD, Rigaku Miniflex II desktop) with Cu-$K_{\alpha 1}$ radiation in the 2θ range of 20°-80°. All the compositions were then sintered at 800 °C in the air with a stay time of 4 hrs. The phases of sintered pellet were determined by XRD to observe the second phase, if any, after firing at higher than calcination

temperature. The specific surface area of calcined powders was determined by BET method through Quantachrome Instruments (ASI-CI-11) of accelerated surface area and porosimetry system using N_2 adsorption-desorption isotherms. The microstructure of the sintered specimens (polished with emery papers) was observed by scanning electron microscope (EVO-Scanning electron microscope MA15 / 18 instrument). The average grain size of each sample was measured by Image *J* software. DSC/TGA was performed using the Perkin Elmer instrument in N_2 atmosphere upto 750 ℃. The room temperature Raman spectra of all four compositions were recorded using Renishaw reflex micro Raman spectrometer. FTIR study was performed in the range of 400 to 4000 cm^{-1} using Perkin Elmer FTIR spectrometer (RXI) in KBr media. Both sides of the pellets were polished and thermally etched to apply the high-temperature Ag paints. The AC impedance data of all four sintered compositions were collected from 200 °C to 600 °C by a Wayne-Kerr LCR meter (6500P) as a function of frequency.

5.3 Results and Discussion

5.3.1 Structural Analysis

Figure 5.1 shows the room temperature X-ray diffractograms of $Na_{0.5}Bi_{0.49}Ti_{(1-x)}Mg_{(x)}O_{3-\delta}$ (x = 0.00, 0.01, 0.02, 0.03) samples. No traces of any secondary phase are observed in the resolution limit of the XRD. All the samples are indexed according to the rhombohedral symmetry and *R*3*c* space group [70]. A weak superlattice reflection present in all the studied compositions at 2θ ~ 38.5º represents the antiphase rotation of TiO_6 octahedra. To observe it very critically, we have also done Rietveld refinement of all the samples using Full Prof Suite package with Pseudo–Voigt peak profile. Figure 5.2 depicts the refinement plots, and the

goodness of fit (χ^2) lies in the appreciable range. Figure 5.1(b) shows the crystal structure of NBT generated using refined cell parameters and vesta software [142].

The variation of lattice parameters is shown in Fig. 5.3(a), and the other refinement parameters are listed in the Table. 5.1.

Figure 5.1: (a) X-ray diffractogram pattern of $Na_{0.5}Bi_{0.49}Ti_{(1-x)}Mg_{(x)}O_{3-\delta}$ (x = 0.00, 0.01, 0.02, 0.03) **(b)** Representative crystal structure in 3D view

It is noticeable that the lattice parameter c increases with Mg^{2+} doping upto 2% of Mg^{2+} doping, i.e. NBT4902 and then after it decreases, whereas lattice parameter a increases up to 1% of Mg^{2+} doping and then decreases. Unit cell volume is also increasing with Mg^{2+} doping upto 2%, as Mg^{2+} (r = 0.72Å) cation have larger radii than that of Ti^{4+} (r = 0.602Å)[191]. Sodium bismuth titanate (NBT) sample possesses local octahedral tilting about the threefold pseudo-cubic axes (a⁻a⁻a⁻) and affects the oxide ion motion in the system [82]. Figure 5.3(b) depicts the variation of octahedral tilting (ϕ) in the sample. This octahedral tilting (ϕ) is due to the bending of TiO_6 octahedra. It is given by the relation:

$$cos^2\Phi = \frac{2-2cos\theta}{cos\theta+5} \qquad (5.1)$$

where ϕ is the octahedral tilting and θ is the bond angle between Ti-O-Ti. The tilting is minimum for NBT4902 sample. The average value of crystallite size and micro-strain was deduced using the Williamson Hall method:

$$\beta cos\Theta = \frac{k\lambda}{D} + 4\varepsilon sin\Theta \qquad (5.2)$$

where β is the line broadening (FWHM), k is the shape factor (k = 0.9), λ is the wavelength of X-ray, D is average crystallite size, ε is strain and Θ is the Bragg's diffraction angle [192]. Estimated values are listed in Table 5.2. It is clear from the table that both the Crystallite size and microstrain are showing the opposite trend, suggesting decrease in the crystallite size and increase in the microstrain with the increase in Mg²⁺ concentration.

Figure 5.2: Rietveld refinement pattern of NBT4900, NBT4901, NBT4902 and NBT4903. Black circles represent the experimental data, and red lines are the fit.

Figure 5.3: **(a)**Variation of lattice parameters *a, c* and, volume **(b)** Octahedral tilting (ϕ) with composition obtained from Rietveld refinement

Table 5.1. Position coordinates and Rietveld fitting parameters and for all the studied samples

Sample	Atoms	Position	coordinates		Wyckoff	R-factor	
		x	y	z	position	Bragg-R factor	Rf factor
NBT4900	Na	0.00000	0.00000	0.26331	6a		
	Bi	0.00000	0.00000	0.26331	6a		
	Ti	0.00000	0.00000	0.02023	6a	4.33	4.19
	O	0.12967	0.34359	0.09193	18b		
NBT4901	Na	0.00000	0.00000	0.27200	6a		
	Bi	0.00000	0.00000	0.27200	6a		
	Ti	0.00000	0.00000	0.02484	6a	3.30	4.37
	Mg	0.00000	0.00000	0.02484	6a		
	O	0.13246	0.34665	0.09369	18b		
NBT4902	Na	0.00000	0.00000	0.27704	6a		
	Bi	0.00000	0.00000	0.27704	6a		
	Ti	0.00000	0.00000	0.02463	6a	4.40	5.21
	Mg	0.00000	0.00000	0.02463	6a		
	O	0.13960	0.35766	0.09583	18b		
NBT4903	Na	0.00000	0.00000	0.28255	6a		
	Bi	0.00000	0.00000	0.28255	6a		
	Ti	0.00000	0.00000	0.01732	6a	5.20	4.17
	Mg	0.00000	0.00000	0.01732	6a		
	O	0.15331	0.37816	0.09762	18b		

Table 5.2: Average crystallite size, micro-strain and density of the investigated compositions

Composition	Average Crystallite size(nm)	Micro-strain	Density (g/cm^3)
NBT4900	41	1.27×10^{-4}	5.2
NBT4901	39	1.72×10^{-4}	5.4
NBT4902	36	1.95×10^{-3}	5.6
NBT4903	34	2.13×10^{-3}	5.6

5.3.2 Migration Pathway Analysis

The bond valance energy landscape for a test oxide ion was calculated using soft-BV software [112]. The energy of oxide ion was calculated for each grid point with the resolution of 0.1Å. Figure 5.4(i) represents the Bond valence energy landscape (BVEL) of all the investigated systems at the iso-surface value of 2.5 eV. On the basis of BVE based calculations, the migration pathways were made for the fully relaxed initial and ending structures (extraneous) from linearly interpolated images. Hence, the oxygen migration energy barrier can be calculated by using the relation, $E_a = E_{max} - E_{min}$, where E_{max} and E_{min} are the highest and the lowest energy iso-surface values along the diffusion pathway of initial and ending structures (extraneous), respectively. The Room Temperature rhombohedral structure was considered in the BVEL calculations [23].

Figure 5.4: (i) Bond valence energy landscape (BVEL) of all the investigated systems at the iso-surface value 2.5 eV. **(ii)** Oxide ion migration channel of studied composition in the b-c plane obtained from BVE method. Presence of yellow surfaces means the presence of the migration pathway channels, and the extraneous iso-surface represents the absence of migration pathways channels

From figure 5.4 (i), it is revealed that at the same iso-surface value, the iso-surface migration channels are more in Mg^{2+}-doped compositions as compared to undoped ones (NBT4900). The BVE landscape for connected and extraneous iso-surface in the b-c plane are shown in Fig. 5.4 (ii). The iso-surface forms a continuous channel along any particular crystallographic direction and reflects the migration energy along that path, and the narrowest path corresponds to the maximum barrier along that channel [193]. Different iso-surface along different orientations suggests anisotropic diffusion in the structure. The energy migration barrier for oxide migration in NBT4900 is ~ 0.68 eV and is found to slightly increase with Mg^{2+} doping, but the number of intermediate pathways segment also increases for Mg^{2+}-doped compositions. Both the stable iso-surface energy and migration energy barrier increases for Mg^{2+}-doped compositions. In perovskites, the anion conduction pathway is assumed to arise by a hopping mechanism wherever migrating anions passes through the bottleneck or opening of the critical radius of a triangle through saddle points which are in between A-site and B-site ions [70]. Here, the migration of oxide ions occurs via edges of TiO$_6$ octahedra via -O1-O1-pathways and through interstitials and saddle points inside the unit cell of the crystal. Further reaction coordinate pathway analysis (Fig. 5.5) also depicts that NBT4900 have less no of intermediate pathway segments for migration as compared to Mg^{2+}-doped compositions. The possible cause for the increase in the migration barrier with Mg^{2+} doping is electrostatic and elastic interaction between dopant and oxygen vacancies. Thus, the oxide-ion migration barriers in NBT and derivative compositions are vastly dependent on the local symmetry's phases, the A- & B-site cation order, tilt configurations and the various oxide-ion diffusion pathways.

Figure 5.5. (a-d) Oxide ion diffusion energy migration barrier landscape for NBT4900, NBT4901, NBT4902 and NBT4903, respectively. All the samples are showing 3D migration channel except NBT4903 in which 2D migration is pre-dominating. The energy barrier is found to be minimum for NBT4900 and increases after doping. Increase in migration barrier for NBT4901, NBT4902 and NBT4903 is attributed to stronger electrostatic interaction between oxygen vacancies and dopant cation. In doped samples, multiple saddle points are formed, and the oxide ion migration takes place through these saddle points and interstitial defects. (e) A representative BVEL of NBT4902 unit cell

5.3.3 Surface Morphology Study

The SEM micrographs of the fractured cross-section are shown in Fig. 5.6. All the samples appeared to be dense, and the results are in accordance with the bulk density measured from the Archimedes density kit (listed in Table 5.2). Although the XRD pattern suggests pure phase sample, SEM micrographs of NBT4903 shows dense phase with some few dispersed particles. The grains consist of non-uniform morphology, and the average grain size was measured using Image *J* software. The grain size is found to increase with Mg^{2+} doping. This increase in the grain size could be attributed to the grain boundary roughening. It is a well-reported fact that oxygen vacancy induces surface and grain boundary roughening as a result of increased entropy [194]. So, the formation of oxygen vacancy may be the reason for grain boundary roughening. Thus, the grain morphology variation also supports the structure-property correlation.

Figure 5.6: (a-d) SEM Micrographs of the sintered samples. Inset shows grain size distribution histogram

5.3.4 FTIR Study

The FTIR spectra of Bismuth deficient and Mg-doped NBT samples in the wavenumber range of 500 cm^{-1} to 4000 cm^{-1} are shown in Fig. 5.7. Characteristic peak located at 3542 cm^{-1} is attributed to stretching of OH group, and the peak at 1640 cm^{-1} is associated with the bending mode of H-O-H. The peak at 2926 cm^{-1} indicates C-H stretching. The sharp band at ~ 630 and 820 cm^{-1} is due to TiO$_6$ octahedra vibration[195]. The band at 820 cm^{-1} shifts with doping as doping forces the octahedron by tilting, and the symmetric stretching process varies with dopant concentration. The band observed at ~ 410cm^{-1} corresponds to the metal-oxide vibration and are the characteristic feature of the perovskite structure[196].

Figure 5.7: FTIR spectrum of Na$_{0.5}$Bi$_{0.49}$Ti$_{(1-x)}$Mg$_{(x)}$O$_{3-\delta}$ (x = 0.00, 0.01, 0.02, 0.03)

5.3.5 Thermogravimetric Analysis

The TGA curve of the studied samples in the temperature range of 30 to 750 °C is shown in Fig. 5.8. An initial increase in mass flow, followed by continuous mass loss, is observed. Multiple kinks at temperature ~ 100, 250 and 460 °C are also observed, showing multistage decomposition reaction. Kink at ~ 100, 250 and 460 °C corresponds to H_2O, O_2 and CO_2 loss, respectively. The peak in the temperature range of 30-150 °C is due to the moisture adsorbed on the surface of particles[190]. As the samples were sintered at high temperature ~ 800 °C, so all the hydrocarbon will get driven off. Further, the X-ray diffractograms of all the samples are also showing clear phase. So we can conclude that the hump at ~100 °C is due to the moisture adsorbed on the powder sample.

The kink observed ~ 520 °C is used to calculate oxygen content in the sample. The oxygen vacancy calculated using the following reaction (Kroger -Vink notation)

$$2Bi_{Bi}^x + 3O_O^x \rightarrow 2V_{Bi}^{''} + 3V_O^{\cdot\cdot} + Bi_2O_3 \tag{5.3}$$

$$MgO \xrightarrow{TiO_2} Mg_{Ti}^{''} + V_O^{\cdot\cdot} + O_O^X \tag{5.4}$$

are listed in Table 5.3. The negative sign represents the oxygen-deficient sample, and the weight loss is mainly because of the loss of lattice oxygen[191]. Mg^{2+}-doped sample is more oxygen-deficient because of the charge compensation.

Figure 5.8: (a-d) TGA of $Na_{0.5}Bi_{0.49}Ti_{(1-x)}Mg_{(x)}O_{3-\delta}$ (x = 0.00, 0.01, 0.02, 0.03) in N_2 atmosphere

Table 5.3: Oxygen vacancy estimated from TGA data and electrical conductivity

Sample	Oxygen deficiency δ	Conductivity (S/cm) at 600 °C
NBT4900	-0.0048	0.084×10^{-2}
NBT4901	-0.0074	0.159×10^{-2}
NBT4902	-0.0919	0.279×10^{-2}
NBT4903	-0.0209	0.129×10^{-2}

5.3.6 Raman Spectroscopy Study

Raman spectroscopy is a sensitive technique to understand crystal symmetry, structural distortion and its relation with doping. Normalized Raman spectrum of the studied samples is

shown in Fig.5.9. The number of Raman modes obtained after deconvoluting the data is as per the Raman modes prescribed by Bilbao Crystallography for R3c symmetry (Fig.5.10). All the modes are broad, showing the polycrystalline nature of the sample. Spectra of all the samples were fitted to Gaussian-like shape using origin software with 13 peaks, and the fitted parameters such as FWHM, Peak intensity, area under the curve were calculated. Major regions observed in the spectrum are categorized as:

Figure 5.9: Room temperature Raman spectra of the studied compositions

1. Band A (80-200) cm^{-1}: It is associated with the Bi-O and Na-O bond and contains three regimes assigned to E(LO1), A$_1$(TO1) and A$_1$(L02) mode [197]. Mode observed at the lower frequency (109-134 cm^{-1}) is usually associated with Bi-O bond because of its higher atomic mass, and the mode observed at higher frequency (155-187 cm^{-1}) is related to Na-O bond[198].

2. Band B (200-400) cm^{-1}: It is associated with the Ti-O vibrations, and it also contains four regimes assigned to A$_1$(TO3), E(TO4), E(TO5) and A$_1$(L05) mode.

3. Band C (400-660) cm^{-1}: It is associated with the vibration of oxygen. Modes observed in this regime are assigned to A$_1$(LO7), E(TO8), and E(LO8).

4. Band D (660-930) cm^{-1}: These bands are associated with the presence of oxygen vacancies and are the most important feature of room temperature Raman spectra. Presence of such a band was first observed by Mineshige et al.[199]. Modes found in this regime are assigned to E(LO9), A$_1$(TO9), and A$_1$(LO9).

To investigate the doping effect on the structure, FWHM and Peak intensity of all the modes were analysed. Figure 5.10 depicts the variation of the FWHM of E(TO4) and E(LO9) modes. With the increases in Mg^{2+} concentration, FWHM of E(LO9) mode increases, suggesting an increase in the oxygen vacancies. Simultaneously there is an increase in FWHM of E(TO4) mode upto 2% Mg^{2+} followed by a decrease for higher doping concentration, suggesting structural distortion in the Ti-O bond of TiO$_6$ octahedra is maximum for NBT4902.

Hence, the interplay between the oxygen vacancies and TiO$_6$ octahedron distortion has appeared, which may affect the conductivity of the specimens with the Mg^{2+} doping.

Figure 5.10: Deconvoluted Raman spectra using 13 peaks showing the presence of R3c symmetry

Figure 5.11: FWHM variation in Raman spectra for E(TO4) and E(LO9) mode of all the investigated compositions

5.3.7 Brunauer- Emmett-Teller (BET) Analysis

Nitrogen adsorption-desorption isotherm as the function of relative pressure is shown in Fig. 5.12. According to IUPAC classification, all the isotherm depicts type IV hysteresis loop and are associated with the mesoporous materials [200] Brunauer, Emmett and Teller (BET) gave the method to determine specific area and porosity given by

$$\frac{1}{\upsilon[(p_0/p)-1]} = \frac{c-1}{\upsilon_m}\left(\frac{p}{p_0}\right) + \frac{1}{\upsilon_m c} \tag{5.5}$$

$$c = exp\left(\frac{E_1 - E_L}{RT}\right) \tag{5.6}$$

$$V_{liq} = \frac{P_a + V_{ads} + V_m}{RT} \tag{5.7}$$

where υ is the volume of adsorbed gas, υ_m is the volume of adsorbed as monolayer, p_0/p is the relative pressure, c is BET constant, E_1 is the heat of adsorption of the first layer, and E_L is adsorption heat for the second and higher layers, V_{liq} is the volume of N_2 in the pore, V_{ads} is the volume of gas adsorbed, V_m is the molar volume of liquid adsorbed, P_a is ambient pressure

and T is temperature [122]. The lower part of the adsorption curve (upto relative pressure 0.2) is used for specific surface area calculation, and the entire adsorption-desorption range is used for pore analysis. Table 5.4 depicts the calculated specific surface area, pore size and volume of the studied composition. The specific surface area of all the samples lies between 100-160 m^2/g. As one can see from table 5.4, the surface area is maximum for NBT4902.

Figure 5.12: BET nitrogen adsorption isotherm as a function of relative pressure

Table 5.4: BET surface area, pore size and pore volume of all investigated compositions

Sample	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
NBT4900	132.9	5.434	0.1806
NBT4901	101.2	22.97	0.5815
NBT4902	158.8	4.626	0.1837
NBT4903	80.75	20.17	0.4072

Above results suggest that the polyol method produces mesoporous NBT material with high specific surface area, indicating its thermal stability. This high surface and low porosity are the important parameters for its application as electrolyte material in solid oxide fuel cells to produce optimum power density.

5.3.8 Electrical Conductivity Study

The representative AC impedance Nyquist plots at 500 °C for all the studied compositions are shown in Fig. 5.13(a). Characteristically, a Nyquist Cole-Cole curve contains three arcs that are usually associated with the grain, grain boundary, and electrode-related impedance responses in high, intermediate and lower frequency regimes, respectively. In the present investigation, a depressed semicircle corresponding to bulk impedance is observed due to the limited frequency range of the equipment. From figure 5.13 (a) it can be seen that the resistance of the sample is decreasing with the increase in Mg^{2+} concentration upto 2% and then after decreases for 3% Mg^{2+} substitution. The Z-view electrical equivalent circuit is also shown in the inset of Fig. 5.13 (a). An equivalent circuit consisting of two parallel combinations of resistance and constant phase element (CPE) was found to best fit the experimental data. The fitting was done in the frequency range of 24Hz-1MHz. Each plot contains two semicircles. The arc at higher frequency corresponds to the grain conduction, and the arc at the lower frequency corresponds to the grain-boundary conduction. The grain-boundary (R_{gb}) and the grain resistance (R_g) are calculated by the intercept of these arcs on the X-axis. Resultant of both R_g and R_{gb} constitute the total resistance of the sample. The total conductivity was calculated taking the bulk responses of the samples using the formula $\sigma_t = \frac{t}{A \times R_t}$ where, σ is the conductivity, R_t ($= R_g + R_{gb}$) is the total resistance, t is the thickness, and A is the area of the pellet. Arrhenius plots for the total conductivity results are shown in Fig. 5.13

(b) for all the compositions. Figure 5.13 (b) is linearly fitted with the Arrhenius relation as per the following equation:

$$\sigma_t T = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \tag{5.8}$$

where σ_0 is the pre-exponential factor, T is temperature, k_B Boltzmann's constant and E_a is the activation energy. The electrical conductivity of NBT4900 is consistent with the earlier reported results of similar systems [93][201]. And on substituting 1-2% of Mg^{2+}, an increase in the conductivity is observed. However, on further adding Mg^{2+} to 3% decreases the conductivity because of the solid solubility limit of the Mg^{2+} on the Ti site, which is ~1-2% [202]. The conductivity may also get lower at higher Mg^{2+}-doping due to the Mg^{2+} defect pair associations leading to a reduced effective concentration of mobile vacancies [203]. The complex formation reaction for this defect pair association could be as follows:

$$Mg''_{Ti} + V_O^{\cdot\cdot} \leftrightarrow (Mg''_{Ti} - V_O^{\cdot\cdot})^\times \tag{5.9}$$

The value of activation energy for the studied samples in the temperature range of 500 - 600 °C are shown in Fig. 5.13(c). Comparison of activation energy suggests that the Mg^{2+}-doped sample shows higher activation energy. Despite the increase in the activation energy, Mg^{2+}-doped bismuth deficient samples are showing higher oxide ion conductivity. The high activation energy for Mg^{2+}-doped compositions is correlated with the migration barrier analysis, as we have discussed in the structural section. A change in activation energy, E$_a$ from ~ 0.7 eV to ~ 0.9 eV above 500 °C to below 500 °C is possibly due to structural transition from tetragonal (T) to cubic (C) phases around this temperature [83]. Although, the room temperature rhombohedral phase is coexisted with tetragonal (T) phases in the temperature range from ~ 250 to ~ 450 °C. For this phase regime, the activation energy may consist of the migration energy along with the association energy of the defect pairs $(Mg''_{Ti} - V_O^{\cdot\cdot})^\times$ and

$(V'''_{Bi} - V^{..}_{O})'$ associates [54]. A similar kind of trend was also observed in the previous literature [91]. This behaviour confirms that the conductivity has to do more with the oxygen ion concentration along with the migration energy barrier[203][204].

Figure 5.13: (a) Representative AC impedance spectra at 500 ºC. Inset in the figure shows corresponding equivalent circuit **(b)**Arrhenius plot for total conductivity. Inset shows the conductivity histogram at 600 ºC **(c)** Variation of migration barrier and activation energy for $Na_{0.5}Bi_{0.49}Ti_{(1-x)}Mg_{(x)}O_{3-\delta}$ (x = 0.00, 0.01, 0.02, 0.03)

The Mg²⁺-substitution at Ti-site in NBT is useful in letting down the resistance responses offered by means of grain boundaries. As the grain boundary contribution is dominated towards the total resistive response of the compositions hence, the total conductivity is also found to

increase with the increase in Mg^{2+}-content in Bi-deficit NBT. Due to this doping effect, more oxygen vacancies are generated. And, thus, a huge amount of oxygen vacancy concentration is accountable for the superior oxide-ion transport inside the grains. Mg^{2+}-substitution reduces the blocking of grain boundaries [205]. Nevertheless, on substitution with more than 2 mol% of Mg^{2+} in Bi-deficit NBT, the bulk conductivity was found to decrease probably due to the association of vacancy-defect pairs and lesser solubility limit of Mg^{2+}. The defect pair complexes $[\,(Mg''_{Ti} - V_O^{..})^{\times}\,]$ formation may decreases the concentration of free oxygen vacancies by acting as internal sink [203][204].

5.4 Conclusion

The present study reports the first time synthesis of Bi deficit Mg^{2+}-doped sodium bismuth titanate perovskite compositions Na$_{0.5}$Bi$_{0.49}$Ti$_{(1-x)}$Mg$_{(x)}$O$_{3-\delta}$ (x = 0.00, 0.01, 0.02, 0.03) via polyol mediated route. This route of preparation helps to produce fine particles, better surface area and good conductivity at relatively lower processing temperatures as compared to the solid-state reaction route. The Mg^{2+} doping at Ti^{4+} site improved the sintering behaviour and also augmented the grain size. The phase formation of the investigated compositions was verified by the X-ray Rietveld refinement techniques confirms the rhombohedral symmetries with *R3c* space group. Structure-property correlation is established to explain the conductivity behaviour of Bi deficient Mg^{2+}-doped sodium bismuth titanate compositions. The oxide ion migration behaviour was analysed by using the Room Temperature X-ray Rietveld refined Crystallographic data. Raman analysis reveals that the conductivity and the octahedron distortion are proportional, and this structural anisotropy helps in the migration. The maximum conductivity was observed for NBT4902 composition over the entire temperature range. Though at higher doping of Mg^{2+} (x > 0.02), the conductivity was found to slightly decrease,

this may be due to the solubility limit of Mg^{2+} and association of Mg^{2+} defect-vacancies pairs. The structural, thermal, micro-structural, textural and migration studies like RAMAN, FTIR, TGA, BET surface area, and ion diffusion pathway analyses are also supported the conduction behaviour of the investigated samples.