

Structural and electrical properties of Barium Titanate (BaTiO_3) and Neodymium doped BaTiO_3 ($\text{Ba}_{0.995}\text{Nd}_{0.005}\text{TiO}_3$)

Tuan Amirah Tuan Sulong^{1,3*}, Rozana Aina Maulat Osman^{1,3}, Mohd Sobri Idris^{2,3} and Zul Azhar Zahid Jamal^{1,3}

¹School of Microelectronics Engineering, University Malaysia Perlis, 02600, Arau, Perlis, Malaysia

²School of Materials Engineering, University Malaysia Perlis, 01000, Kangar, Perlis, Malaysia

³COE Frontier Material Research Centre, School of Material Engineering, University Malaysia Perlis, 01000, Perlis, Malaysia

Abstract. Barium titanate (BaTiO_3) and Neodymium (Nd) doped BaTiO_3 with composition $\text{Ba}_{0.995}\text{Nd}_{0.005}\text{TiO}_3$ were prepared using conventional solid state reaction method to study the dielectric properties of materials. Pure phase samples were found at final heating temperature of 1400 °C for overnight. X-ray diffraction analysis reveals the changes in the lattice parameter and unit cell volume of the pure perovskite tetragonal structure with space group ($P4mm$). Electrical analysis is carried out to investigate the dielectric properties, conductivity behaviour and dielectric loss of BaTiO_3 and $\text{Ba}_{0.995}\text{Nd}_{0.005}\text{TiO}_3$. $\text{Ba}_{0.995}\text{Nd}_{0.005}\text{TiO}_3$ have a broaden dielectric peaks with high permittivity of 8000 and reasonably low loss $\tan \delta$ which is about 0.004 (1 kHz).

1 Introduction

Dielectric ceramics are widely used in advance microelectronics technologies such as capacitor and microwave communication [1]. A high dielectric constant ceramic had received a lot of attention in reducing the size of the microelectronics circuits where high permittivity and low dielectric loss are required for many electronics application. BaTiO_3 composition modified by doping have been extensively studied for high dielectric materials applications.

In previous work reported by Shaikh & Vest [2], BaTiO_3 structure are very sensitive to the doping level and will change the electrical behaviour of pure BaTiO_3 . In order to improve the properties of BaTiO_3 , some modifications on BaTiO_3 structure was made and rare earth materials were of interest due to a huge improvement in the permittivity as reported by Abdul Hamid et. al. [3] in Lanthanum (La) doped BaTiO_3 and Samarium (Sm) doped BaTiO_3 by Ganguly et al. [4].

Neodymium (Nd) doped BaTiO_3 was previously studied by other researcher, however, in this study, we present a simple study about the physical behaviour and electrical behaviour change by small amount of Nd doping to the A-site perovskite of BaTiO_3 . The trivalent Nd is very interesting to study because it previously reported that small amount of Nd will exhibit a PTCR effect and change the electrical behaviour from insulating to semiconducting [5]. Instead of that, in term of structure, the radius of Nd^{3+} (1.27Å) is very close to the radius of Ba^{2+} (1.61Å) and small size of Ti^{4+} (0.605Å) at the center

of the octahedral site towards one of the other corner oxygens. In view of the radius, it is possible for Nd^{3+} to enter into the A-sites of BaTiO_3 perovskite and effect the properties of BaTiO_3 ceramics. In this work, the phase analysis, structural analysis and electrical behaviour of BaTiO_3 and $\text{Ba}_{0.995}\text{Nd}_{0.005}\text{TiO}_3$ was presented. The incorporation location of small amount of doping Nd doped to BaTiO_3 was identified using Rietveld Refinement analysis.

2 Experimental Procedure

High purity of raw materials BaCO_3 (99%), TiO_2 (99%) and Nd_2O_3 (99%) from Sigma-Aldrich were used as starting materials. Stoichiometric amount of materials were mixed and grounds using pestle and mortar. Samples were pressed uniaxially using handpress into pellets and heated at final temperature of 1400 °C for 12 hours with heating rate 5°C/min. The phase purity of the samples were analyzed using the X-ray Diffraction (XRD: D2-ADVANCE, Bruker, Germany) from 2θ , 20°-130°. Structural studied obtained were refined using the General Structure Analysis Software (GSAS). For impedance measurements, pressed pellets were sintered at 1400°C for 6 hours. Silver paste was used as electrode. Samples was painted with silver paste on both pellets' surfaces. Pellets were connected to the Platinum (Pt) leads of a conductivity jig which was mounted inside a horizontal tube furnace. Impedance data were recorded on a stepwise heating cycle using HIOKI IM 3522 Impedance Analyzer instrumentation in frequency range 10 Hz to 100 kHz.

* Corresponding author: rozana@unimap.edu.my

3 Result and Discussion

Figure 1 shows the XRD patterns of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃ respectively. The reflection patterns of Ba_{0.995}Nd_{0.005}TiO₃ remain similar as BaTiO₃ sample, except with the presence of broad peak at 2θ: 22° and 51° respectively. All samples of the BaTiO₃ and Nd-doped BaTiO₃ were indexed with tetragonal phase with the unit cell $a = 3.9937 \text{ \AA}$, $c = 4.0342 \text{ \AA}$ and $a = 3.9964 \text{ \AA}$, $c = 4.0288 \text{ \AA}$, volume = 64.38 \AA^3 and volume = 64.34 \AA^3 respectively. The space group belong to P4mm. Figure 2 shows the variation of lattice parameters and unit cell volume of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃.

Introducing the small amount of Nd content into pure BaTiO₃ at A—sites perovskite structure, resulting the changes as shown in Figure 2(a) and 2(b). A decrement in the lattice parameter and unit cell volume was observed. The decrement in lattice parameter and unit cell volume means that the lattice is shrinkage and the size of the unit cell become smaller. This effect is might be due to the size incompatibility of Nd with ionic radii of Nd³⁺ and Ba²⁺, thus causes an overall shrinkage of unit cell and volume.

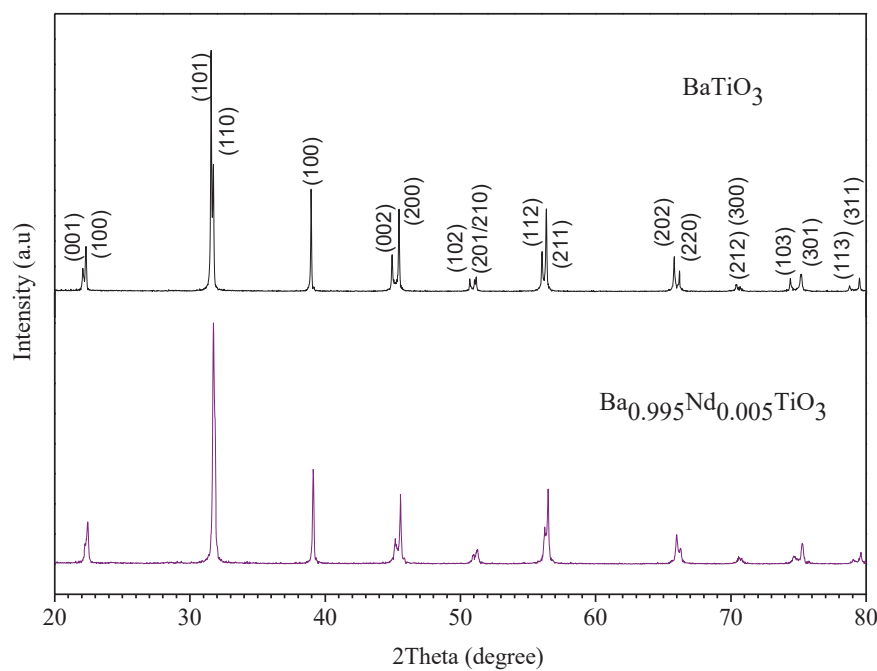


Fig.1. Indexed XRD patterns of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃

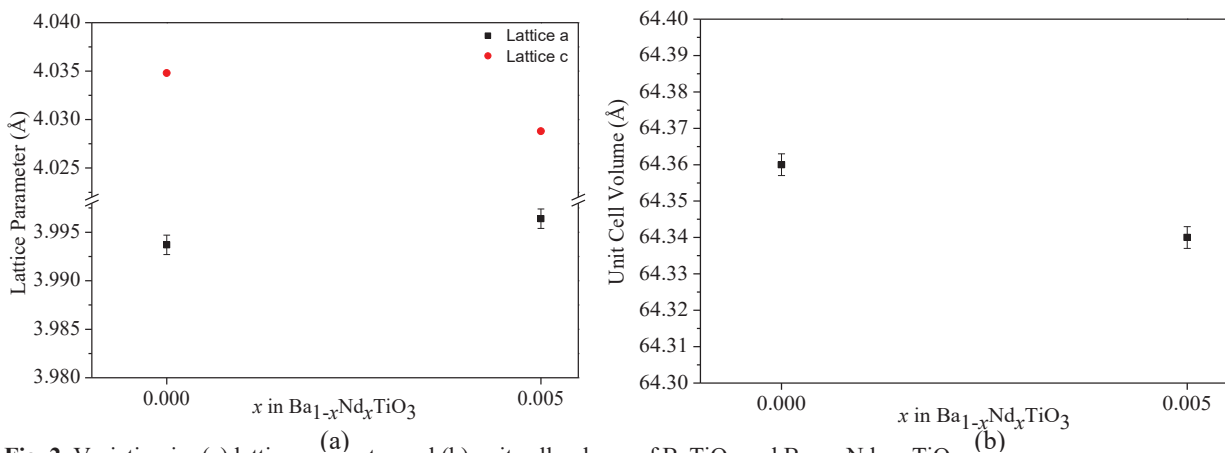


Fig. 2. Variation in: (a) lattice parameter and (b) unit cell volume of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃.

XRD data for Ba_{1-x}Nd_xTiO₃ (0 ≤ x ≤ 0.015) were collected and the structure was refined using the atomic coordinates of tetragonal perovskite (ICSD No: 245945) as starting parameters. The cation site occupancies were varied with Ba and Nd on A—sites and Ti on B—sites. The

optimized parameters for refinement were detailed in [6,7]. The refinement result, Table 1, shown the substitution of Nd into BaTiO₃. Reliability refinement parameters show relatively lower R_p, R_{wp} and χ². This result give some ideas to claim that substitution

mechanism, suggest by the refinement result are mostly reliable. Fitting parameters (R_p and R_{wp}) indicate acceptable agreement between refined and observed XRD patterns for $BaTiO_3$ and $Ba_{0.995}Nd_{0.005}TiO_3$ ceramics with both tetragonal structure. Some variations in occupancy values were showed due to the replacement of Ba atoms by Nd atoms which indicates that (Ba or Nd) atoms located in the same A-site occupy the same site in a fractional percentage. Note that there are small variations in atomic positions related to the titanium and

oxygen atoms while the barium and neodymium atoms keep their fixed positions within the structure. Figure 3(a–d) shown the difference profile of (a) $BaTiO_3$ and (b) $Ba_{0.995}Nd_{0.005}TiO_3$ after refinement. Results obtained by using the Rietveld refinement method indicate acceptable agreement between observed XRD patterns and fitted theoretical results. This indicate the success of the Rietveld refinement method which displays small differences near zero in the intensity scale.

Table 1. Refinement data for $BaTiO_3$ and $Ba_{0.995}Nd_{0.005}TiO_3$.

Doping Concentration	$x = 0$	$x = 0.005$
Ti, z	0.5171 (3)	0.5126 (2)
Ba (1a), U_{iso}	0.3841 (8)	0.0052 (7)
Nd (1a), U_{iso}	-	0.0076 (9)
Ti (1b), U_{iso}	0.5740 (7)	0.0050 (9)
O1(1b), U_{iso}	0.8923 (9)	0.0064 (5)
O2 (2c), U_{iso}	0.2377 (5)	0.0118 (9)
R_{wp}	14.04	13.89
R_p	10.44	11.04
χ^2	3.994	4.468

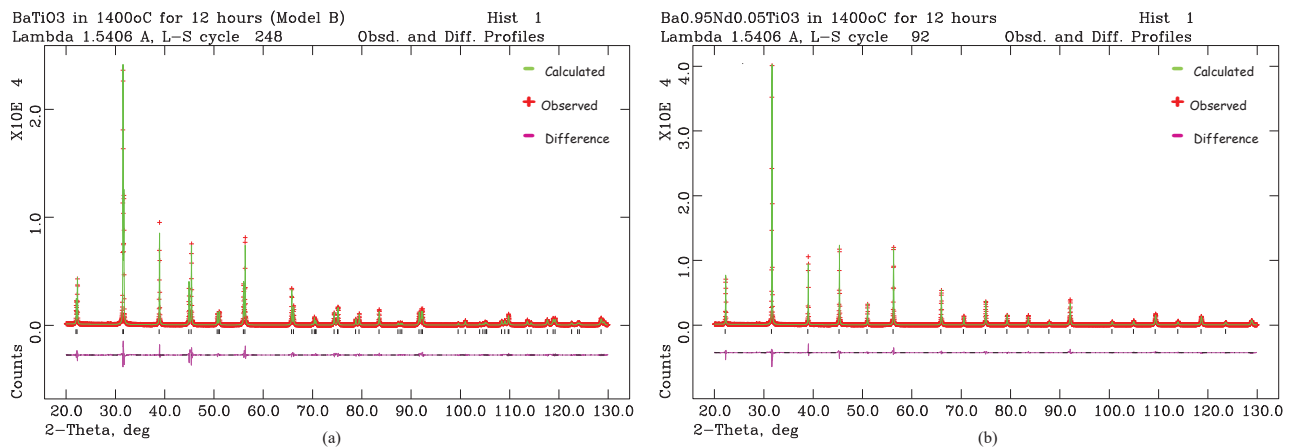
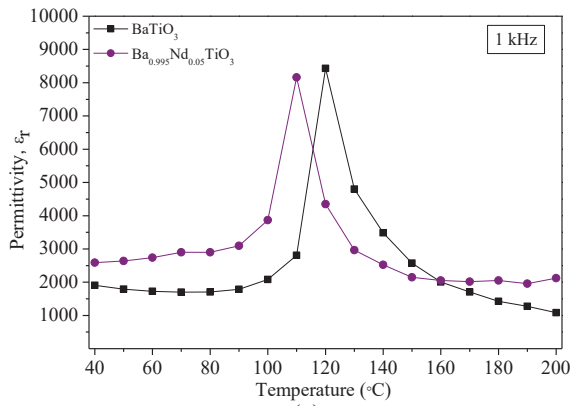


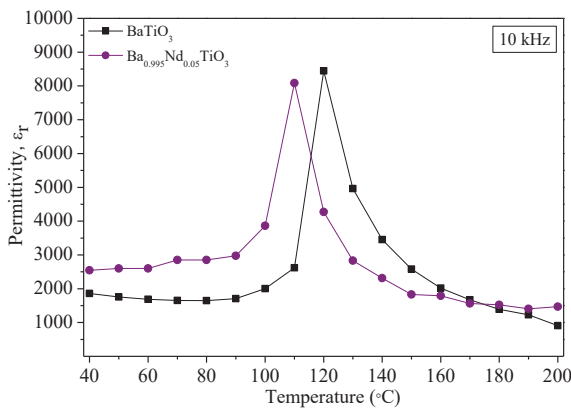
Fig. 3. Structural refinement plot for a) $BaTiO_3$ and b) $Ba_{0.995}Nd_{0.005}TiO_3$

Permittivity at fixed frequency of 1 kHz, 10 kHz and 100 kHz for $BaTiO_3$ and $Ba_{0.995}Nd_{0.005}TiO_3$ sintered at 1400 °C for 6 hours are shown in Figure 4 respectively. Data show sharp maximum permittivity for all samples in accordance with literature. Permittivity at T_c was remarkably decreased for Nd-doped $BaTiO_3$ as compared to undoped $BaTiO_3$. Maximum permittivity for pure $BaTiO_3$ about 8500, at curie temperature (T_c) of 120 °C, while for Nd-doped $BaTiO_3$, permittivity at T_c are 8000, 5000 and 2000 at different frequency. At room temperature, the permittivity of Nd-doped $BaTiO_3$ show remarkable value as compared to permittivity of $BaTiO_3$. Small amount of Nd shows a very interesting result by shifting the T_c towards lower temperature, and slight decreament in permittivity change at T_c . This might be related to the high dipole polarisation of rare-

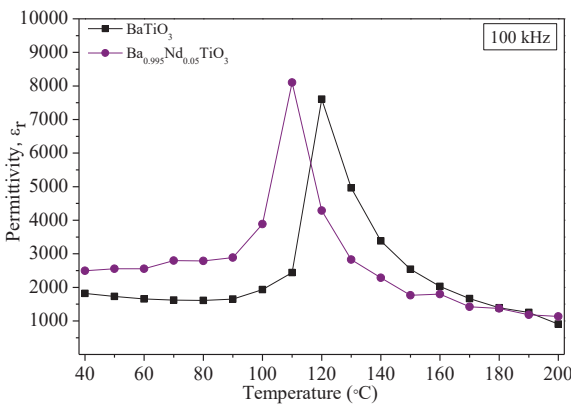
earth based-Nd, microstructure and grain size of the sample. The permittivity reaches a peak at the Curie point and falls of at higher temperatures in accordance with the Curie–Weiss law [8]. This phenomena were strongly related with the shifting of maximum permittivity at T_c of Nd-Doped $BaTiO_3$ at tetragonal phase to cubic phase above T_c . Generally, in heavily doped $BaTiO_3$ ceramics grain size is usually suppressed and the permittivity of $BaTiO_3$ ceramics attains the maximum when the grain size is 1 μ m or less[9]. Factors that influence permittivity include type of dopant, doping mechanism, processing conditions and grain size [10]. On the other hand, high permittivity may be associated with sample geometry and, in particular, with thin layer effects associated with grain boundaries, surface layers or sample-electrode contacts [11].



(a)

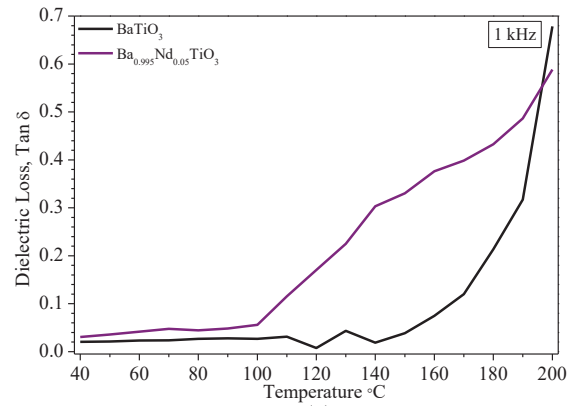


(b)

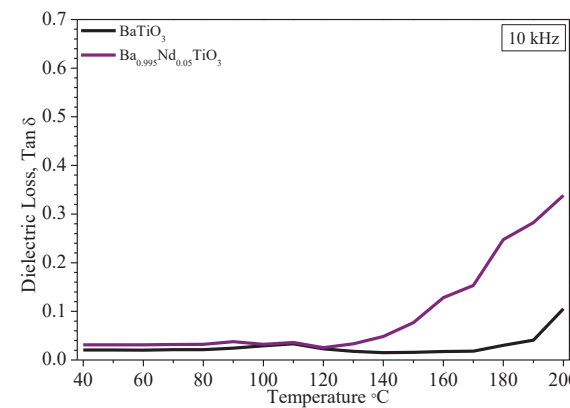


(c)

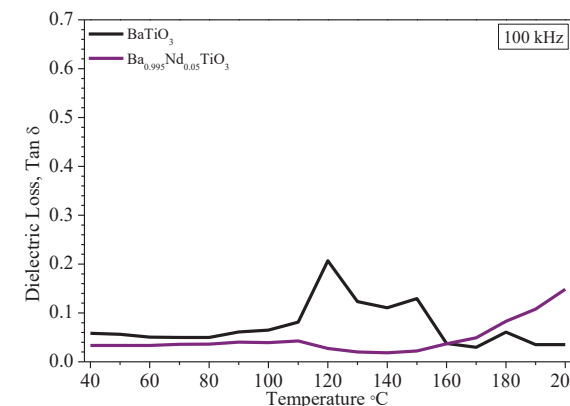
Fig. 4. Temperature dependence permittivity of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃ at (a) 1 kHz, (b) 10 kHz and (c) 100 kHz respectively.



(a)



(b)



(c)

Fig. 5. Frequency dependence of dielectric loss BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃ of (a) 1 kHz, (b) 10 kHz and (c) 100 kHz respectively.

Figure 5 shows the temperature dependence in dielectric loss of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃ at a frequency of 1 kHz. The dielectric loss of the Ba_{0.995}Nd_{0.005}TiO₃ is very low at much lower temperature which is below 0.04 loss. The dielectric loss of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃ at frequency of 1 kHz is very low below T_c and increase a little bit to 0.06 about T_c. However the loss was very minimal as frequency increased in Figure 5(b) and 5(c). Minimum dielectric loss as low as 0.2 was maintained at lower temperature, however, rapidly increased at high temperature. By doping Nd, below T_c, the dielectric loss was bound from 0.04 to 0.004. Figure 6 (a) and (b) shows the frequency dependence conductivity of BaTiO₃ and

Ba_{0.995}Nd_{0.005}TiO₃ at frequency of 1 kHz, 10 kHz and 100 kHz sintered at 1400°C for 6 hours. The conductivity of BaTiO₃ changes with the frequencies of 1 kHz to 100 kHz. At 1 kHz, the conductivity is about 5.4x10⁻⁸ Scm⁻¹. However a small increase of 10⁻⁷ Scm⁻¹ at 10 kHz and increased again at 100 kHz to 10⁻⁶ Scm⁻¹. The conductivity at T_c for BaTiO₃ is higher compared to other temperatures and much higher at higher frequency. The conductivity of Ba_{0.995}Nd_{0.005}TiO₃ tend to increase from 10⁻⁸ to 10⁻⁶ Scm⁻¹ approaching T_c at 110°C.

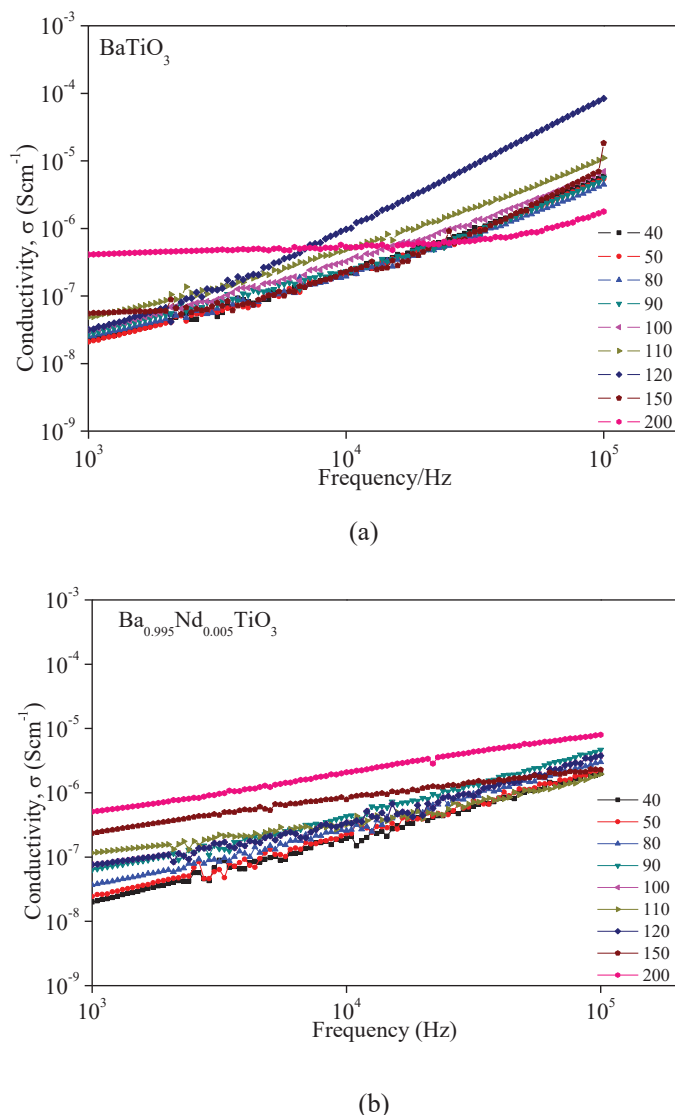


Fig. 6. Frequency dependence of conductivity of (a) BaTiO₃ and (b) Ba_{0.995}Nd_{0.005}TiO₃

The range of conductivity at low frequency of 1 kHz and 100 kHz were about $9.0 \times 10^{-7} \text{ Scm}^{-1}$ and $1 \times 10^{-5} \text{ Scm}^{-1}$ respectively. The conductivity difference considered high, with two orders of magnitude. This is in agreement with the exact conductivity of a semiconductor material, correlated with the observed properties and related phenomenon responsible [10]. Therefore, conductivity was greatly affected by temperature and frequency of range 1 kHz to 100 kHz. Data collection was limited to frequencies < 1 MHz, due to increases in inductive effects that influenced the impedance data [11].

4 Conclusion

The effect of Nd incorporation to the A-sites of perovskite BaTiO₃ was studied. This effect is seen by observing the lattice and volume change

in the structure of BaTiO₃ with percentage 0.68% of shrinkage. However, the structure was still maintain with tetragonal unit cell and the structural site of Nd was confirmed by rietveld analysis with Nd at A-sites. The permittivity maximum was at T_c with 8500 and reduced to 8000 by doping at low frequency. However at room temperature, the substitution of Nd show a very high permittivity compared to pure BaTiO₃ at three different frequencies. The conductivities of BaTiO₃ and Ba_{0.995}Nd_{0.005}TiO₃ increased by increasing the frequency and temperature.

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