

Research Article

PHYSICS**Structural and Dielectric Properties of Sodium-Doped BaTiO₃ Ceramics Synthesized via Tartrate Precursor Technique****Haidy M. Ragab^{*}, Osama M. Hemed, Mohamed M. Salem**

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Corresponding author:* Haidy M. Ragab*E-mail:* haidy.mostafa@science.tanta.edu.egReceived:** 26/9/2024**Accepted:** 16/10/2024**KEY WORDS**

BaTiO₃ ceramics,
Sodium doping,
Dielectric
properties,
tartrate precursor
method

ABSTRACT

This study investigates the influence of sodium (Na) doping on the electric and dielectric properties of tetragonal barium titanate (BaTiO₃) ceramics, specifically within the composition Ba_{1-x}Na_xTiO₃ (BNT) where $x = 0, 0.2, 0.4, 0.6$. BNT ceramics were synthesized using the tartrate precursor technique. Structural characterization of the synthesized samples was performed using Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM). The FTIR spectra confirmed the successful formation of the composite samples, with TEM analysis corroborating the presence of a uniform tetragonal crystal structure across all compositions. A single-phase formation was consistently observed, indicating the stability of the tetragonal structure upon Na doping. The dielectric properties, particularly dielectric loss, were systematically analyzed as a function of temperature under various frequencies. The results demonstrate significant changes in the dielectric behaviour with increasing Na content, suggesting potential applications of Na-doped BaTiO₃ in tunable dielectric devices and contributes to the understanding of doped BaTiO₃ ceramics for their application in advanced electronic materials.

Introduction

Ferroelectricity in Rocksalt was first discovered by Valsek in 1921. Since the identification of barium titanate (BaTiO₃), research on ferroelectric materials has made significant strides. In the 1950s, lead-based ceramics found extensive use in piezoelectric transducers and capacitor applications, driving advancements in the field (Leschhorn et al., 2012). Since then, numerous relaxor ferroelectrics, such as lead magnesium niobate (PMN), and ferroelectric ceramics like lead titanate (PbTiO₃), lead zirconate titanate (PZT), and lead lanthanum zirconate titanate (PLZT), have been discovered, thoroughly investigated, and implemented in a wide range of device applications (Valasek, 2011; Darwish et al., 2024)

Ceramics, which are compounds formed by both metallic and non-metallic elements, are typically synthesized under high pressure and temperature. These materials exhibit characteristics such as chemical stability, wear resistance, brittleness, and susceptibility to thermal shock (Valasek, 2011; Leschhorn et al., 2012). The evolution of thin-film technologies and ceramic processing techniques has been pivotal in advancing ferroelectric ceramics, particularly for dielectric applications (Valasek, 2011;

Leschhorn et al., 2012; Munir et al., 2021). These innovations have fueled growing interest in ceramic composites for industrial, optical, and medical applications (Dragoi et al., 2011; Munir et al., 2021). Dielectric ceramics, in particular, possess high permittivity, excellent thermal stability, low dissipation, and resistance to high temperatures (Dragoi et al., 2011).

Barium titanate (BaTiO₃) remains one of the most important ferroelectric materials, widely used in the production of ceramic components for microelectronic devices such as actuators, piezoelectric transducers, positive temperature coefficient resistors (PTCR), and multilayer ceramic capacitors (MLCC), among others. The ferroelectric properties of BaTiO₃ arise from spontaneous polarization, which occurs upon cooling to a specific temperature, known as the Curie temperature ($T_{\text{Curie}} = 120\text{--}130^\circ\text{C}$). At this point, BaTiO₃ undergoes a phase transition from a cubic to a tetragonal structure (Leschhorn et al., 2012; Salem et al., 2024).

Recent years have seen growing interest in the development of Ba_(1-x)Na_xTiO₃-based ceramics due to their enhanced electrical properties. Barium sodium titanate (BNT) is a notable member of

the BaTiO₃ family, known for its potential in various applications (**Chen et al., 2014**). BaTiO₃ (BTO) belongs to the ABO₃ perovskite-type ferroelectric family (where A = Ba and B = Ti), characterized by 12- and 6-fold coordination of oxygen in its crystal structure. BaTiO₃ offers two primary sites for substitution, referred to as the A-site (Ba²⁺) and the B-site (Ti⁴⁺). Various additives are introduced to BaTiO₃ to optimize performance, control grain size, and enhance electrical properties. Common dopants include Sr²⁺, Ca²⁺, Sn⁴⁺ and Na⁺. Notably, sodium (Na⁺) exhibits superior chemical stability, and its incorporation into BaTiO₃ has been shown to improve both electrical and dielectric characteristics (**Vijatović et al., 2008; Dragoi et al., 2011; Salem et al., 2024**).

In this study, Ba_(1-x)Na_xTiO₃ (BNT) was synthesized using the tartrate precursor method. The influence of Na⁺ substitution at varying concentrations on the morphology, structure, and ferroelectric properties of BNT was systematically investigated (**Vijatović et al., 2008; Dragoi et al., 2011**).

Sodium doping in BaTiO₃ (BNT) has demonstrated promising results in tuning dielectric behavior, making these materials highly suitable for use in advanced electronic devices. Specifically, the observed stability of the

tetragonal phase and the modifications in dielectric loss behavior highlight the potential of Na-doped BaTiO₃ ceramics in tunable dielectric devices, capacitors, and other electronic components requiring precision and stability under variable conditions. These findings not only advance the fundamental understanding of doped BaTiO₃ ceramics but also position them as critical materials for next-generation microelectronic and optoelectronic applications.

Experimental details

Ferroelectric Ba_{1-x}Na_xTiO₃ (BNT) ceramics with varying sodium concentrations (x = 0, 0.2, 0.4, 0.6) were synthesized through the tartrate precursor method. The starting materials-barium nitrate (Ba(NO₃)₂), sodium carbonate (Na₂CO₃), and titanium dioxide (TiO₂)- were used in precise stoichiometric ratios corresponding to the desired Na content. The Ba, Na, and Ti solutions were thoroughly mixed and stirred for 15 minutes using a magnetic stirrer on a hot plate. To ensure uniformity, an aqueous solution of tartaric acid (C₂H₄O₆) was added, and continuous stirring was maintained.

The solution was then heated at 80°C to gradually evaporate the solvent while stirring continued until a dry mixture was achieved (**Vijatović et al., 2008**;

Chen et al., 2014). This dried mixture underwent additional drying at 180°C for two hours to remove any remaining moisture. The final perovskite structure was formed by annealing the powder at 1000°C for four hours (Vijatović et al., 2008).

Subsequent to annealing, the powder was compressed into tablets using a mechanical compressor with a pressure of 5000 kg cm⁻². The thickness of each tablet was controlled, yielding thickness measurements of 0.362, 0.265, 0.38 and 0.451 cm for x = 0, 0.2, 0.4 and 0.6 respectively.

The synthesized samples were characterized using Fourier transform infrared (FTIR) spectroscopy at room temperature with a PerkinElmer 1430 instrument, covering a wavenumber

range of 400 cm⁻¹ to 4000 cm⁻¹. Additionally, transmission electron microscopy (TEM) was used to determine the particle sizes of the samples.

Result and discussion

FTIR analysis

Figure (1) illustrates the FTIR absorption spectra of BaTiO₃, Ba_{0.8}Na_{0.2}TiO₃, Ba_{0.6}Na_{0.4}TiO₃, and Ba_{0.4}Na_{0.6}TiO₃ powders. The IR spectrum of pure BaTiO₃ displays four prominent absorption bands. Notably, the band observed at 640 cm⁻¹ is attributed to the Ti-OIII bending vibration and the stretching vibrations of TiO₆ octahedra, which are integral to the BaTiO₃ crystal structure (Mudinepalli et al., 2013; Salem et al., 2024).

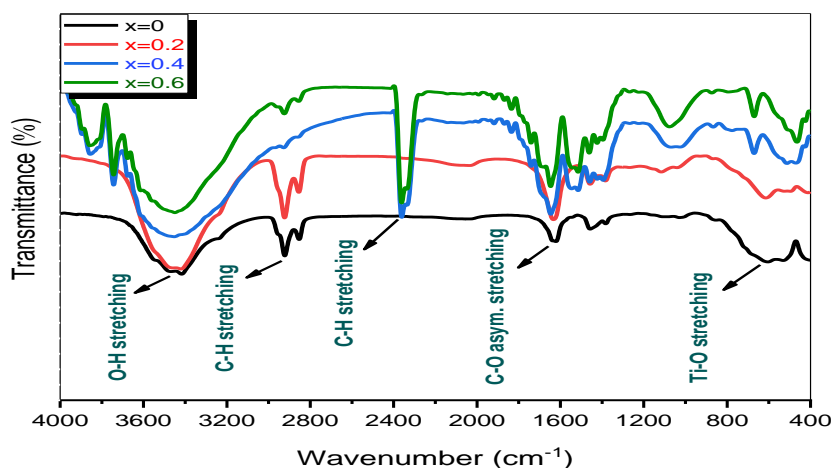


Fig. (1): FTIR of spectra of composite samples Ba_{1-x}Na_xTiO₃ where (x = 0, 0.2, 0.4, 0.6)

During the synthesis of BaTiO₃, the interaction with tartaric acid is reflected by a peak at 1641 cm⁻¹, corresponding to the asymmetric C-O bond vibration. The initial two absorption bands are linked to the stretching and bending vibrational modes of Ti-O. Furthermore, the

absorption band at 2368 cm⁻¹ is attributed to the asymmetric and symmetric C-H stretching vibrations of the CH₂ group, with additional C-O deformation vibrations also observed near 1641 cm⁻¹.

Table (1): The values of the main frequencies (ν_1 and ν_2) and the force constants (F_1 and F_2)

X	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$F_1(\text{dyn/cm})$	$F_2(\text{dyn/cm})$
0	603.98	402.83	258080.8886	114803.2922
0.2	614.72	412.19	267340.9064	120200.3224
0.4	670.57	469.19	318125.8572	155742.8882
0.6	675.07	465.19	322409.8835	153098.6885

Table (1) presents the main frequency bands (ν_1 and ν_2) of Ba_{1-x}Na_xTiO₃ samples with varying Na content, along with their respective force constants (F_1 and F_2). The peak at 1641 cm⁻¹, corresponding to the C-O asymmetric Stretching vibration, is associated with the BaCO₃ phase. As the Na content increases, this behavior can be attributed to changes in bond length within the structure. The force constants for the A and B sites of the perovskite structure were calculated using the following equation (Mudinepalli et al., 2013).

TEM analysis

Figure (2) presents Transmission Electron Microscopy (TEM) images of BNT synthesized via the tartrate precursor method with Na content varying ($x = 0, 0.2, 0.4, 0.6$). The figure

also includes the corresponding electron diffraction patterns for these samples. The TEM images reveal a progressive evolution in nanocrystallite sizes, ranging from 7.93 nm to 32.64 nm, as a function of increasing Na content (Mudinepalli et al., 2013; Salem et al., 2024).

Table (2): Average grain size of Ba_{1-x}Na_xTiO₃ ($x=0, 0.2, 0.4, 0.6$)

X	Grain size (nm)
0	10.01
0.2	11.04
0.4	18.46
0.6	22.49

The average crystallite size exhibits a complex dependence on the Na content. As Na content increases, a decreasing trend in size is observed. In the absence of Na ($x = 0$), the crystallite size reaches

its maximum, which suggests a stabilizing effect exerted by the Ba-rich matrix. However, as Na content increases to $x = 0.6$, a gradual reduction in size is observed, attributed to the

smaller ionic radius of Na⁺¹ compared to Ba²⁺. This ionic substitution likely affects the structural arrangement, contributing to the observed size decrease.

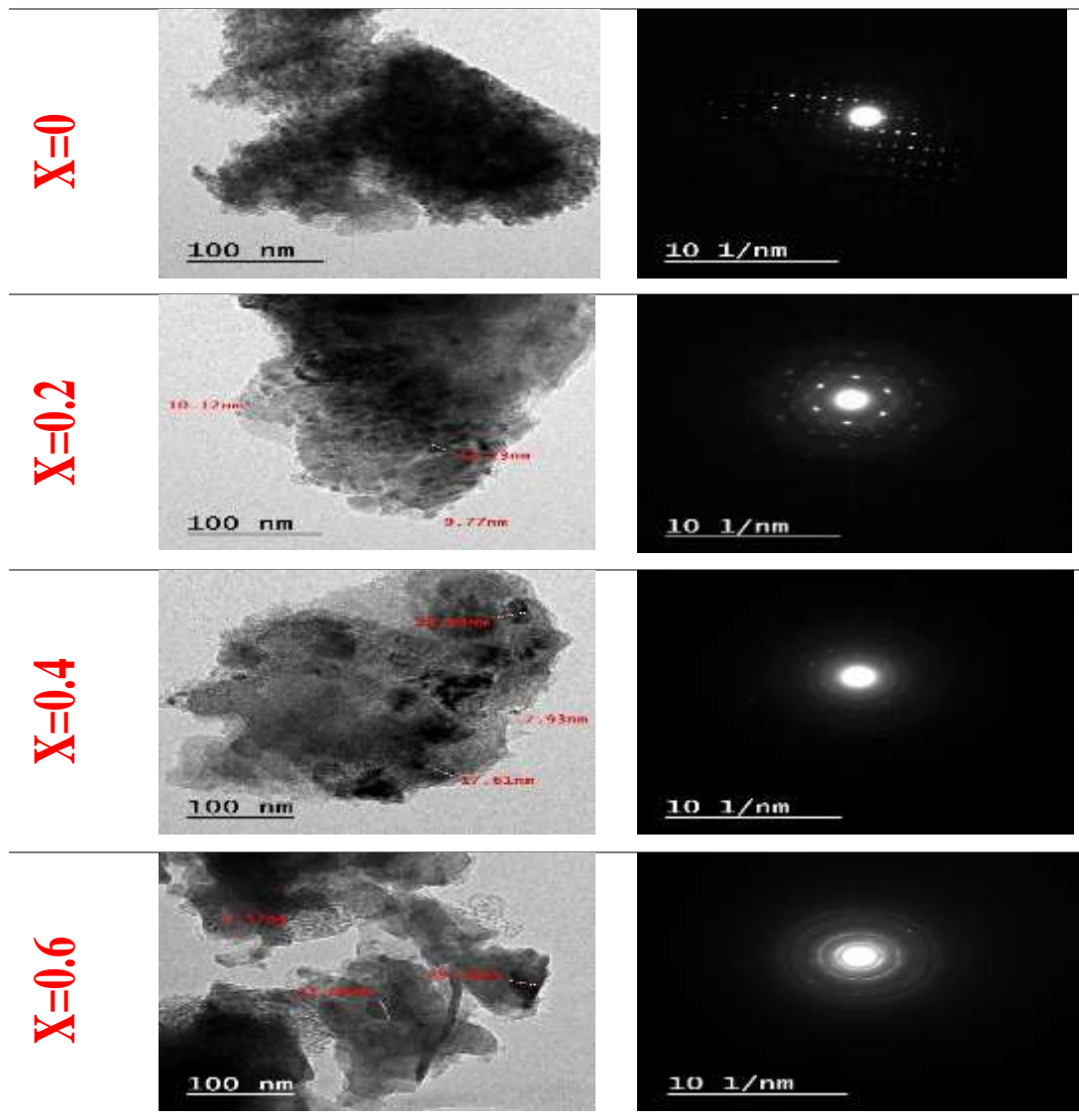


Fig. (2): TEM images of Ba_{1-x}Na_xTiO₃ ($x = 0, 0.2, 0.4, 0.6$)

In addition to the TEM analysis, selected area electron diffraction (SAED) patterns were shown in **Fig. (2)**, further confirm the crystallinity of the synthesized BNT powders. These

diffraction patterns align with the characteristic tetragonal structure of perovskite-type materials. The material's nanocrystalline structure is demonstrated by the concentric halo

rings visible in the electron diffraction patterns (Mudinepalli et al., 2013). The presence of bright spots within these rings suggests a high level of crystallinity, reflecting coherent scattering from well-organized regions within the material (Mudinepalli et al., 2013).

Dielectric properties

Figure (3) illustrates the variation of the dielectric constant as a function of temperature for $Ba_{1-x}Na_xTiO_3$ with different sodium content ($x = 0, 0.2, 0.4, 0.6$) at fixed frequencies of (50, 100, 150 and 200 kHz). It is observed that the sample with $x = 0.6$ exhibits the lowest dielectric constant across all measured frequencies, while the samples with $x = 0, 0.2$ and 0.4 display the highest dielectric constant values. At lower temperatures, the dielectric constant remains relatively stable and independent of room temperature. However, as the temperature increases beyond a certain threshold, the dielectric constant shows a noticeable rise (Liu et al., 2021; Hussein et al., 2023).

The dielectric constant is calculated by

$$\epsilon' = \frac{c_p d}{\epsilon_0 A}$$

Where d is the thickness of pellet sample, c_p is the capacitance, ϵ_0 is the

permittivity of free space, and A is the cross-sectional area of the pellet (Vuong et al., 2020).

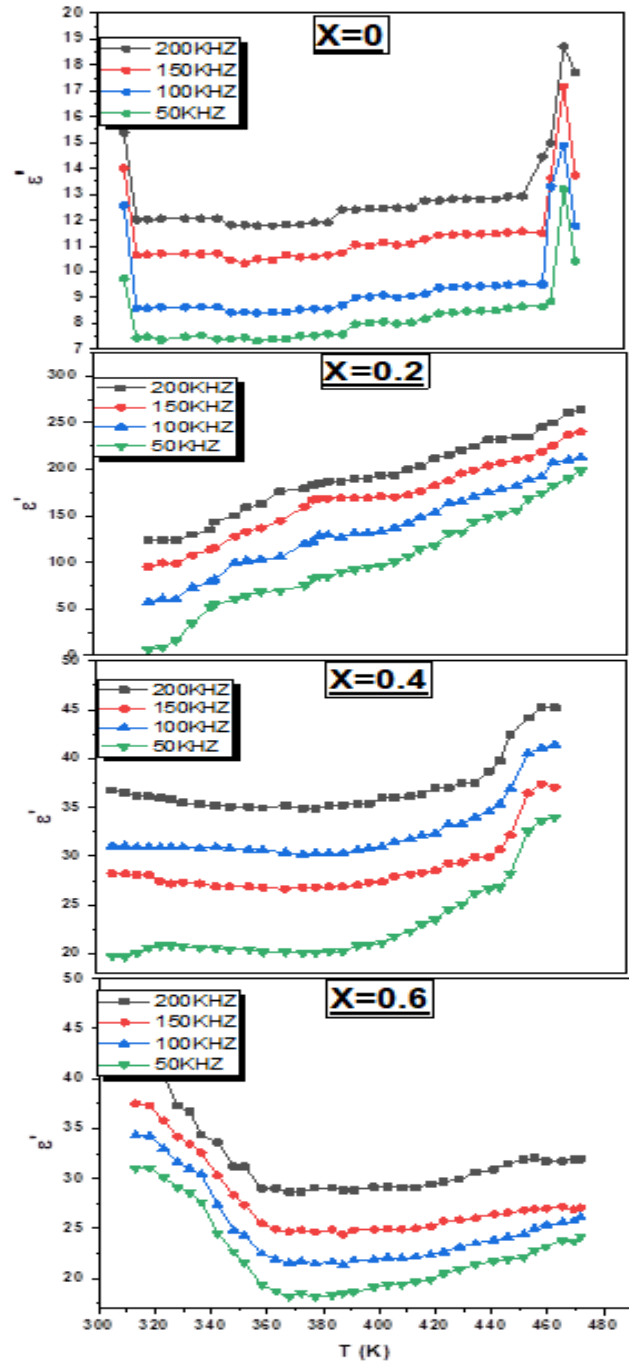


Fig. (3): Dielectric constant of $BaTiO_3$ doping by Na content

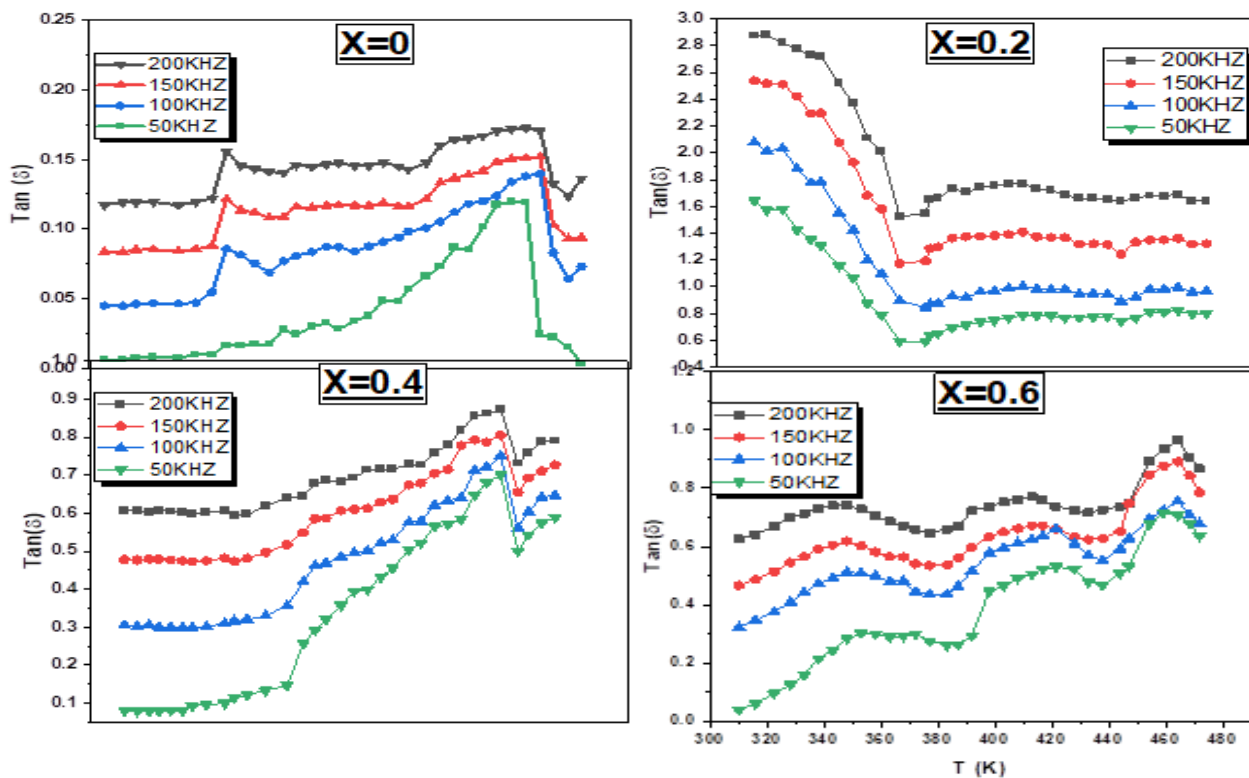


Fig. (4): Dielectric loss $\text{Tan}(\delta)$ as a function of $T(\text{K})$ for different Na content

Figure 4 displays the dielectric loss ($\text{Tan}(\delta)$) for all samples at various frequencies (50, 100, 150, 200 kHz). It is observed that the sample with $x = 0.2$ exhibits the lowest dielectric loss across all frequencies, while the samples with $x = 0, 0.4,$ and 0.6 show higher dielectric loss values.

Ac conductivity

Figure 5 illustrates the variation of AC resistivity for $\text{Ba}_{1-x}\text{Na}_x\text{TiO}_3$ as a function of reciprocal temperature ($1000/T$) at different frequencies (50, 100, 150 and 200 kHz). At higher temperatures, AC resistivity is observed to decrease with rising temperature, indicating that the thermal activation of charge carriers

enhances their mobility, leading to a reduction in resistivity (Yakout, 2020; Hussein et al., 2023). The Curie temperature marks the point at which this relationship changes, corresponding to the transition of the sample from ferroelectric (or ferromagnetic) to paraelectric (or paramagnetic) behavior (Zeng et al., 2006; Yakout, 2020). It is also noted that as both temperature and frequency increase, AC resistivity decreases. This can be attributed to electron hopping between Ti^{3+} and Ti^{4+} ions under the influence of the applied electric field, which facilitates conduction (Tomar et al., 2020; Yakout, 2020).

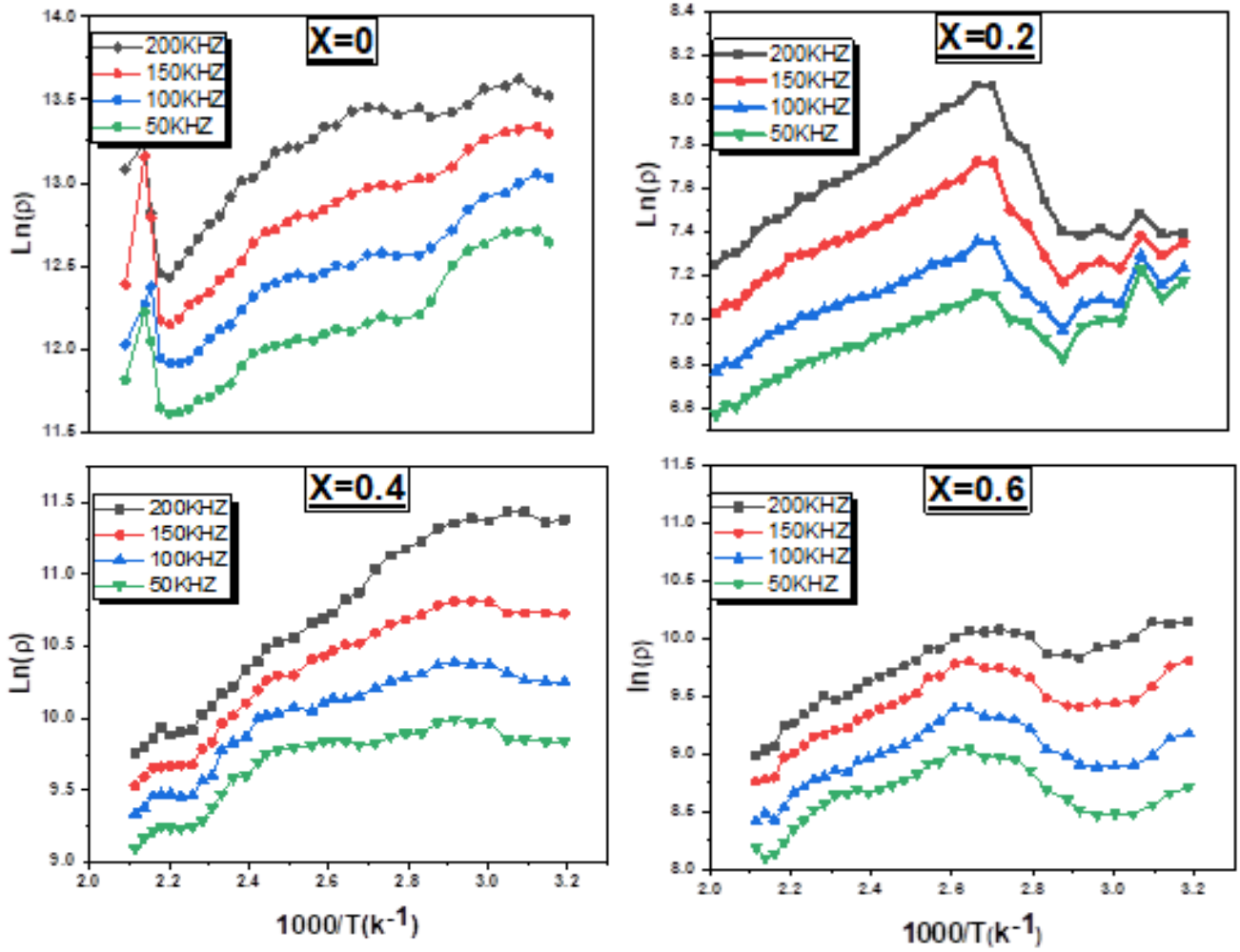


Fig. (5): $\ln(\rho)$ vs. $1000/T(K)$ for BNT samples at different Na content.

The material exhibits a negative temperature coefficient of resistance, as evidenced by the consistent reduction in AC resistivity with increasing temperature (Mudinepalli et al., 2013; Tomar et al., 2020; Salem et al., 2024). The relation among temperature and resistivity may be written as:

$$\rho = \rho_0 \cdot \exp\left(\frac{\Delta E}{K_B T}\right)$$

where ρ is resistivity at temperature T , ΔE is the electrical process activation energy,

and K_B the Boltzmann constant that has a defined value of 1.380649×10^{-23} .

Conclusion

This study has successfully elucidated the impact of sodium (Na) doping on the electrical and dielectric properties of tetragonal barium titanate (BaTiO_3) ceramics, specifically within the composition $\text{Ba}_{1-x}\text{Na}_x\text{TiO}_3$ (BNT) for $x = 0, 0.2, 0.4,$ and 0.6 . The synthesis of BNT ceramics using the tartrate precursor technique resulted in a consistent single-phase formation with a

stable tetragonal crystal structure, as confirmed by Fourier transform infrared (FTIR) spectroscopy and transmission electron microscopy (TEM) analysis. Significant changes in dielectric behavior were observed with increasing Na content, particularly in terms of dielectric constant and dielectric loss, which were systematically analyzed as a function of temperature and frequency. These findings highlight the potential for Na-doped BaTiO₃ ceramics in tunable dielectric devices, underscoring their applicability in advanced electronic materials. Furthermore, the understanding gained from this research contributes to the broader knowledge of ferroelectric ceramics and paves the way for future studies aimed at optimizing the performance of such materials for various technological applications.

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الخصائص الهيكلية والعازلة لسيراميك BaTiO₃ المطعم بالصوديوم الذي تم تحضيره عبر تقنية السلائف الطرطرية

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تبحث هذه الدراسة في تأثير منشطات الصوديوم (Na) على الخواص الكهربائية والعازلة لسيراميك تيتانات $x = 0$ ، 0.2 ، حيث $Ba_{1-x}Na_xTiO_3$ (BNT) تركيبة ضمن وتحديدًا، BaTiO₃ الزوايا رباعي الباريوم 4.0 ، 6.0 تم تصنيع سيراميك BNT باستخدام تقنية السلائف الطرطرية. تم إجراء التوصيف الهيكلي للعينات المركبة باستخدام التحليل الطيفي بالأشعة تحت الحمراء لتحويل فورييه (FTIR) والمجهر الإلكتروني النافذ (TEM) ، أكدت أطياف FTIR التكوين الناجح للعينات المركبة ، مع تحليل TEM الذي يؤكد وجود بنية بلورية رباعية الزوايا موحدة عبر جميع التركيبات. لوحظ باستمرار تشكيل أحادي الطور ، مما يشير إلى استقرار الهيكل الرباعي مع التطعيم بعنصر Na . تم تحليل خصائص العزل الكهربائي وخاصة فقدان العزل الكهربائي ، بشكل منهجي كدالة لدرجة الحرارة تحت ترددات مختلفة. تظهر النتائج تغييرات كبيرة في سلوك العزل الكهربائي مع زيادة محتوى Na ، مما يشير إلى التطبيقات المحتملة ل BaTiO₃ المطعم Na في الأجهزة العازلة القابلة للضبط ويساهم في فهم سيراميك BaTiO₃ المطعم لتطبيقها في المواد الألكترونية المتقدمة.