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Enhanced structural and electrical properties of copper-substituted Lead Zirconate Titanate ceramics using impedance spectroscopy for device applications

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Abstract:

The use of doping lead zirconate titanate (PZT) derived from ceramics with copper (Cu) has been extensively researched because of its considerable effect on the physicochemical properties of the materials. This paper analyzes recent advances in understanding the effects of Cu doping on PZT material, focusing on structural changes, electrical characteristics, and dielectric behavior. $\text{Pb}_{1-x}\text{Cu}_x\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocomposites were synthesized by the sol-gel method. The XRD analysis and Rietveld refinement showed the formation of either mixed-phase tetragonal and rhombohedral structures via R3m and P4mm space groups. SEM micrographs revealed irregular, dense grains, with the average grain size decreasing as the Cu rate increased. The dielectric constant as a function of temperature presents dielectric resonance phenomena. We also studied the activation energy and Cole-Cole curves. The characteristic pattern of the impedance spectra shows semicircular arcs that change with increasing temperature, in addition to a negative thermal coefficient of resistivity (NTCR) for $x=0.00$ up to $x=0.05$ and a positive thermal coefficient of resistivity (PTCR) for $x=0.075$ in ceramics. The activation energy increases with relatively higher Cu levels.

Keywords: PZT, ceramics, impedance spectra, activation energy, Cole-Cole, PTCR, NTCR

Introduction

In today's electronics and communications technologies, creating new materials with improved electrical and dielectric properties is essential for many applications. In practice, lead zirconate titanate (PZT)- based ceramics are prominent in materials research and engineering because of their excellent piezoelectric, ferroelectric, and dielectric properties[1][2]. These ceramics are widely used in sensors, micro-motors, actuators, ultrasonic cleaning, transducers, and capacitors[3], [4], [5], [6]. This material has been developed in different forms: thin films, nanorods, nanoparticles, and nanotubes [7][8][9], [10], [11]. At the Zr/Ti = 0.52/0.48 ratio, the PZT phase diagram is defined by a near-right morphotropic phase boundary (MPB). In this region, the MPB is defined by the combination of two distinct crystallographic phases (typically rhombohedral and tetragonal) [12], [13]. PZT has a very high piezoelectric response and is also distinguished by excellent dielectric properties at this phase boundary, stable over a wide range of temperatures[14][15]. To further improve the performance of PZT composites, researchers have made various modifications using different dopants (donor and acceptor), which exist as

two cationic forms and an ionic oxygen site. They can affect the microstructure, phase composition, and, consequently, the electrical and dielectric characteristics of ceramics. The incorporation of transition metals (Mg, Mn, Fe,...) into the PZT system is being investigated across several publications[16][17][18]. Nitu Kumari et al. synthesized $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-x}\text{Fe}_x\text{O}_3$ through the conventional solid-state route using various Fe^{3+} doping concentrations and analyzed their properties[19]. The X-ray diffraction patterns in this study show a tetragonal crystal structure and a decrease in tetragonality and unit cell size with increasing dopant concentration. SEM micrographs indicate that doping concentration ($x > 0.05$) induces a decrease in grain size. Prasenjit Prasad Sukul et al. previously investigated PbZrTiO_3 ceramics doped with $\text{Er}^{3+}/\text{Yb}^{3+}$. They demonstrated how the sensitivity curve's dependence on energy spacing suggests that changing one of these will rapidly alter the sensitivity's properties[20]. Benya Cherdhirunkorn and colleagues utilized the mixed oxide processing method to produce Co-doped PZT ceramics. They demonstrated that XRD analyses confirm that implanted N^+ ions can cause deformities in structure and/or changes in the favored orientation due to a change in the ferroelastic domain in the near-surface area, and the dielectric characteristics exhibited decreases in both relative permittivity[21]. The structural and electrical properties of the Er^{3+} -doped PZT 52/48 have been studied by Jaime Alberto Sanchez Cacere et al. Electrical evaluation of the ceramics showed a peculiar ferroelectric-paraelectric phase transition at a predicted temperature of 390°C , and the typical grain size declined with increasing erbium content.[22]. With the sol-gel process, M. Prabu et al. created PZT (52/48) electroceramics and examined their structural and electrical characteristics. The study illustrates the uneven distribution of particles caused by granulation-induced aggregated particles on the surface. The researchers established the activation energy of the sample to be 0.210 eV by analyzing the Arrhenius diagram of direct current conductivity compared against the reciprocal of absolute temperature [23]. In our studies, we focus mainly on the microstructural, electrical, and dielectric property characterizations of Cu-doped PZT-based ceramics with the formula $\text{Pb}_{1-x}\text{Cu}_x\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PCxZT), investigating how the Cu dopant affects their properties. The main objectives of this study are, firstly, to synthesize Cu-modified PZT ceramics and to assess the electrical properties, most notably the conductivity and impedance spectroscopy. Additionally, to evaluate dielectric properties such as the permittivity of dielectric materials as a function of temperature. Processes of energy activation in these modified ceramics are also discovered and examined in order to discover the mechanisms underlying their improved performance. The ceramics' microstructure and phase evolution will be investigated using characterisation techniques including conventional X-ray diffraction (XRD), Raman analysis, and scanning electron microscopy (SEM). The aforementioned electrical properties and conductivity measurements will be carried out to analyze the effect of doping with Cu on the charge transfer mechanisms of the ceramics. Impedance spectroscopy will provide insight into the electrical response over a range of frequencies and will help clarify factors such as grain boundary impacts and polarization dynamics. Dielectric properties, including permittivity, will be thoroughly examined in order to comprehend the effect of Cu doping on the potential of ceramics to maintain and release electrical energy.

Materials and methods

The reagents were obtained via the sol-gel technique utilizing lead acetate [$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$], zirconium acetate [$\text{Zr}(\text{CH}_3\text{CO}_2)_4$], titanium alkoxide [$\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$], and copper acetate [$\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$] as initial precursors. All produced powders were

mixed stoichiometrically according to the formula $\text{Pb}_{1-x}\text{Cu}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, with $x = 0.00, 0.025, 0.05$, and 0.075 . The resulting substance underwent milling and calcination processes at 700°C for 4 hours. The heated PCxZT-based powders were combined with water that was distilled and polyvinyl alcohol (PVA), dried in a drying oven to form pellets of approximately 12 mm in diameter and 1 mm in thickness, and then sintered at 1100°C for 4 h. The phases of preparation are delineated in the literature relevant to our work [18], [24], [25].

Results and discussion

XRD Studies:

Figure 1 shows X-ray diffraction diffractograms of PCxZT samples ($x = 0.00, 0.025, 0.05$, and 0.075) taken at ambient temperature after calcination at 700°C for four hours. Each specimen is composed of a pure perovskite phase. Based on the results, the pure and doped samples confirmed that the data align with the rhombohedral and tetragonal structures associated with the $R3m$ and $P4mm$ space groups, respectively [25]. The formation of these two phases is caused by the morphological phase boundary (MPB) of lead zirconate titanate [i.e., $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$] [26][27]. XRD diagrams reveal an expansion of the peaks, which suggests the presence of nanoparticles in the nanometer range. The size of the crystallite of the nanocrystalline PCxZT powders annealed at 700°C was calculated using the Scherrer equation. Size of crystallite $= k\lambda/\beta\cos\theta$ which k is the proportionality constant (Scherrer constant), which is typically determined as 0.9; λ is the wavelength of the X-ray and is $1.54060 \text{ \AA}$; θ is half of the angle (2θ) of diffraction; and β is the widened value of the (110) line at its entire width of half maximum (FWHM) in radians. Figure 2 shows the variation in crystallite size calculated for different PCxZT compositions. We chose the most resolved peak (110), which lies approximately at the angle $2\theta=31$. Based on this figure, the shift in grain size relative to the percentage of Cu doping is non-linear. The size of the crystallite relatively decreases with increasing copper doping level, demonstrating that the addition of Cu causes the grain size in the PZT material to decrease. These changes may be a result of the effect of the dopant (copper) on the dynamics of grain formation. They could also be linked to effects on the microstructure of the material, affecting its mechanical and electrical properties. In the literature, the same results have already been reported [16][20][28].

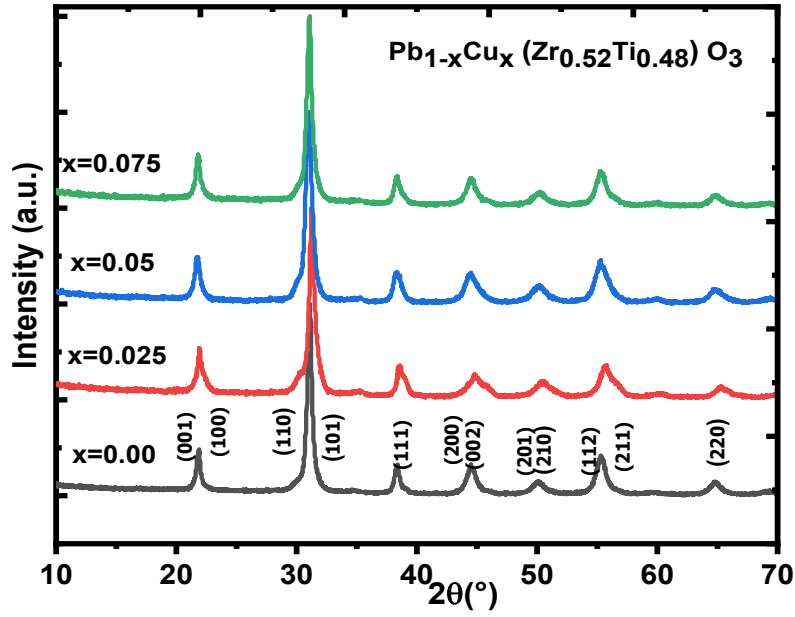


Figure 1: Powder X-ray diffraction patterns of PCxZT samples calcined at 700 °C

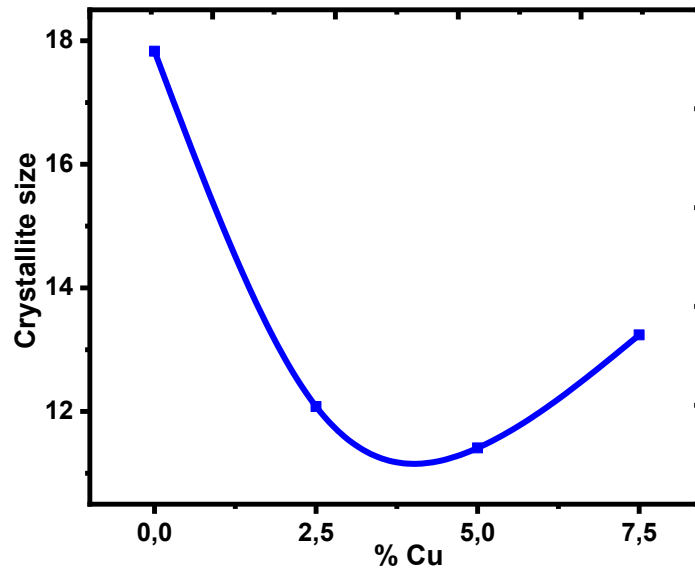


Figure 2: Evolution of crystallite size of PCxZT powders with Cu content

Raman Spectroscopy

Figure 3 shows the room-temperature Raman spectra of the PCxZT powders for $x = 0.00, 0.025, 0.05$, and 0.075 , covering the $100\text{--}1000\text{ cm}^{-1}$ range. In the undoped sample ($x = 0.00$), eight bands stand out clearly: $203, 274, 331, 507, 552, 597, 717$, and 775 cm^{-1} . Group theory predicts $3A_1 + B_1 + 5E$ modes for this structure, and all of them show up here, assigned to $E(2TO), E+B_1, A_1(2TO), E(3TO), E(4TO), A_1(3TO), E(4LO)$, and $A_1(3LO)$, in that order. The $E+B_1$ mode is worth noting; its presence points to tetragonal and rhombohedral symmetries coexisting in the lattice [29]. Near 507 cm^{-1} sits the $E(TO_3)$ mode, which comes from symmetric O-Ti-O stretching inside the $[TiO_6]$ octahedra[30][12]. For the reference sample, these values align well with those reported by Buixaderas et al. [31] and Deluca et al.[12] Once copper enters the picture, the same bands are still there; nothing disappears, but their intensities shift depending on how much Cu was added. Take the $A_1(2TO)$ mode: it strengthens as x increases, indicating

more tetragonal phase formation. This mode also drifts toward lower wavenumbers as x rises from 0.00 to 0.075, and past that point the shift picks up pace. E(3TO) and A1(3TO) move around too, depending on copper content. Put together, these spectral changes track the structural disruption caused when Cu^{2+} ions swap in for Pb^{2+} , Zr^{4+} , or Ti^{4+} , matching what the XRD data already showed, and consistent with prior literature [32].

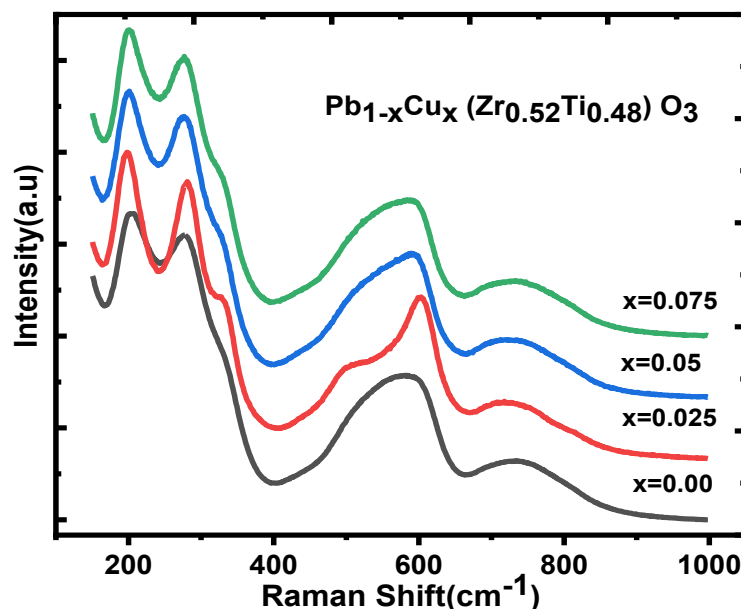
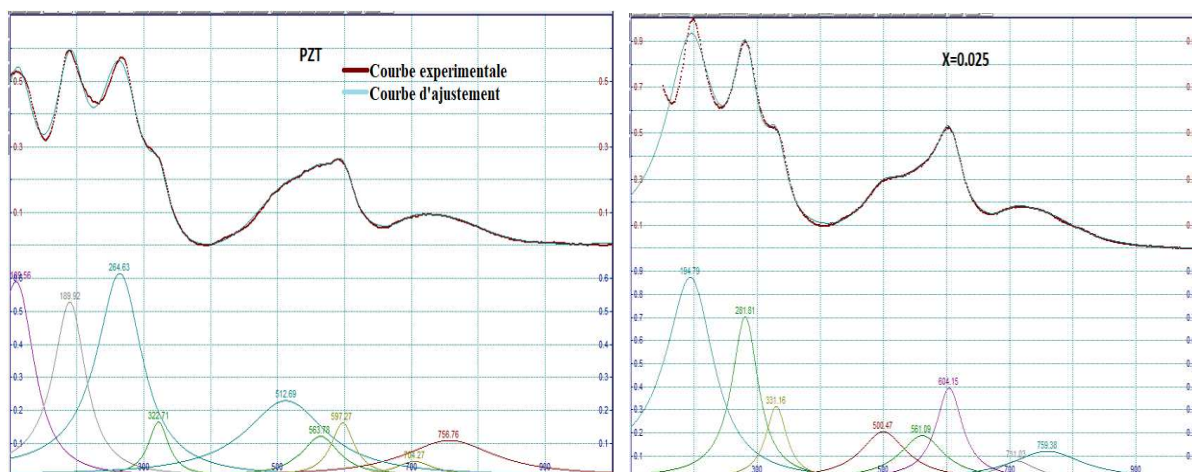


Figure 3: Room-temperature Raman spectra for PCxZT ceramics

The software “Peakfit” is used to adjust the Raman spectra, as shown in Figure 4. The central position and the half-width calculated at half-maximum of the different Raman bands are outlined in Table 1. Based on these observations, all the Raman frequencies of the PCxZT powders are shifted with the C content. In reality, the modes shift to higher frequencies. The change may be due to replacement of a light atom (Cu (63.54)) by a heavy atom (Ti (47.86)) or substitution of a heavy atom (Cu (63.54)) by a light atom (Pb (207.2) or Zr (91.22)).



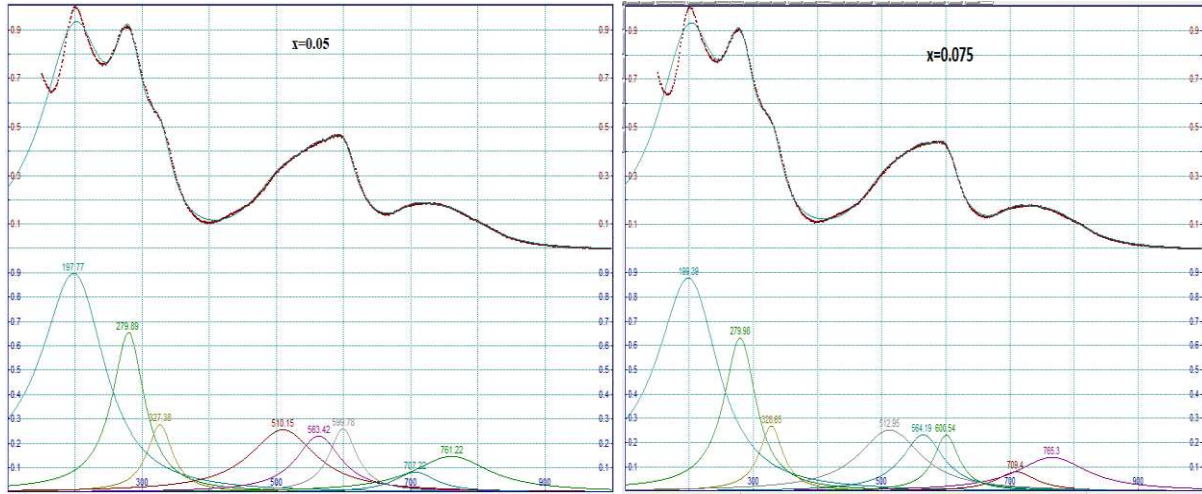


Figure 4: Fitting RAMAN spectra using Peakfit software for PCxZT ceramics

Table 1: Positions and width at half-height of the active Raman bands for PCxZT powders

Modes	x= 0.00	x= 0.025	x= 0.05	x= 0.075
E(T2O)	189.92	194.79	197.76	199.39
	F=59	F=94	F=119	F=119
E+B1	264.63	281.81	279.89	279.98
	F=83	F=51	F=59	F=61
A1(T2O)	322.71	331.81	327.37	326.85
	F=37	F=40	F=45	F=44
A1(T3O)	597.27	604.15	599.77	600.54
	F=42	F=51	F=50	F=47
A1(L3O)	756.76	759.38	761.22	765.3
	F=166	F=138	F=138	F=134

SEM studies: To study product morphology and particle size, conventional scanning electron microscopy images of PCxZT samples were collected and shown in Figure 5. The micrograph of the PCxZT ceramics reveals irregular and dense grains with the presence of small spherical grains. All ceramics show varying distributions of grain size. The Cu doping of PZT material influences a consequently the mean grain size of the ceramics. The variation in the grain size of PCxZT ceramics formed at 1100°C/4h as a function of Cu level is illustrated in Table 2. The grain size of the substance ranges from 3.76 μm to 3.71 μm with the increasing content of Cu from 0% to 7.5%. However, the overall trend appears to be a gradual reduction in grain size with increasing Cu content. The observed differences in grain size at different levels of Cu may indicate changes in the grain nucleation density. In addition, there is a significant relationship between the material's mechanical characteristics and the grain size[33]. By reducing the displacement of dislocations and increasing resistance to mechanical strain, smaller grains may strengthen the material[34].

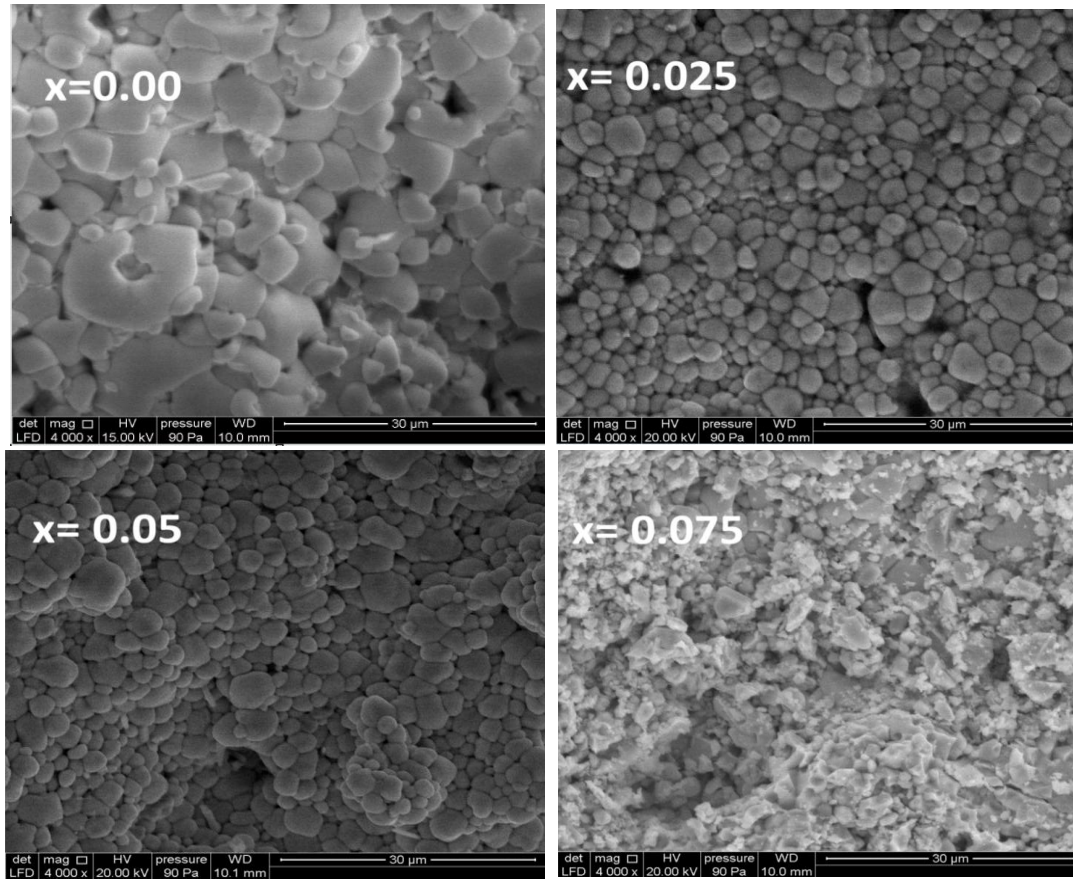


Figure 5: SEM of PCxZT ceramics for different values of $x = 0, 0.025, 0.05$ and 0.075

Table 2: Average grain size of PCxZT ceramics sintered for four hours at 1100°C

Value of x	Average grain size (μm)
0.00	3.76
0.025	3.72
0.05	3.79
0.075	3.71

Dielectric Properties

Temperature-dependent dielectric constant (ϵ_r)

Figure 6 illustrates the variations in the dielectric constant of the examined ceramics as a function of temperature at elevated frequencies ($f > 1$ MHz). For all ceramics, the values of dielectric permittivity were observed to rise initially with elevated temperature, reach a zenith at the maximum dielectric constant (ϵ_{max}) at the optimum temperature (T_m), and then decline. Conversely, all formulations demonstrated a decrease in the dielectric constant with rising frequency. The majority of polar dielectrics have this characteristic[35]. In addition, the maximum dielectric constant moves in the direction of lower temperatures as the frequency increases, which is an indication of the phenomenon referred to as dielectric resonance[18], [33], [36]. The observed phenomenon is believed to result from the temporal interactions between a fluctuating external electromagnetic field and the electric charges within a dielectric

substance. The variations of T_m and $\epsilon_{\max}$ at frequencies demonstrated that all frequencies exhibit identical characteristics. The peak dielectric constant swiftly diminishes, exhibiting fluctuations with increased Cu concentration. This is possibly attributable to the replacement of Pb and the replacement of Cu for Ti/Zr.

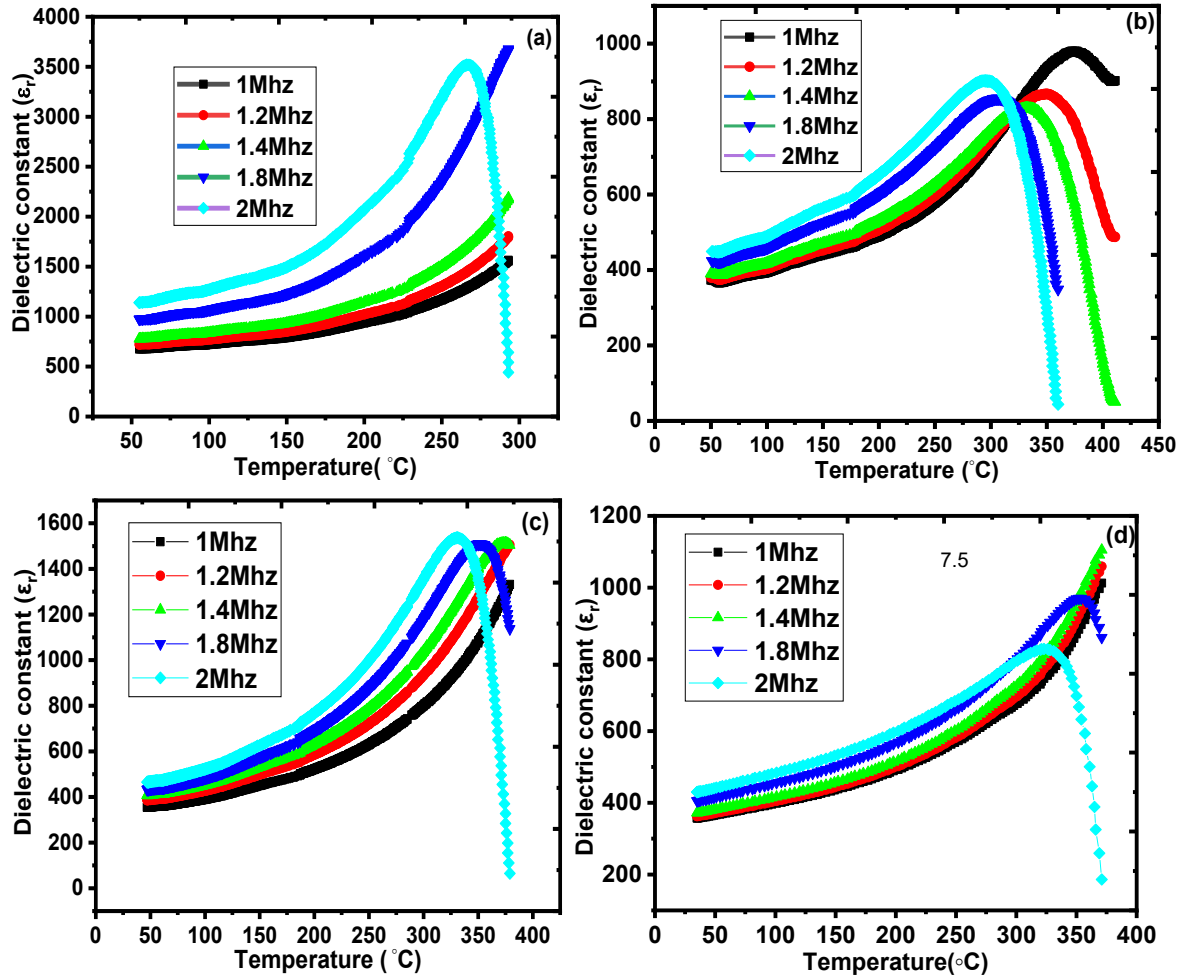


Figure 6: Dielectric Constant as a Function of Temperature for PC_xZT Ceramics at Various Frequencies

Dielectric losses: Dielectric losses of PC_xZT ceramics as a function of temperature at various frequencies are displayed in Figure 7. Numerous temperature-dependent and frequency-dependent anomalies may be seen in the curves. At temperatures below 300 $^{\circ}\text{C}$ for pure PZT and 350 $^{\circ}\text{C}$ for doped samples, the variation exhibits nearly constant dielectric losses. Then, they rise quickly as the temperature rises until it reaches a maximum value, following which they fall quickly and become almost constant. The rise in dielectric capabilities could be caused by a process of charge carrier dispersal or relaxation at low frequencies[37]. The maximum dielectric losses increase toward lower temperatures as frequency rises. The PZT behaves similarly for sample sizes with the other values of x . On the other hand, electrical losses are highly frequency-dependent; they rise at some frequencies and decrease at others.

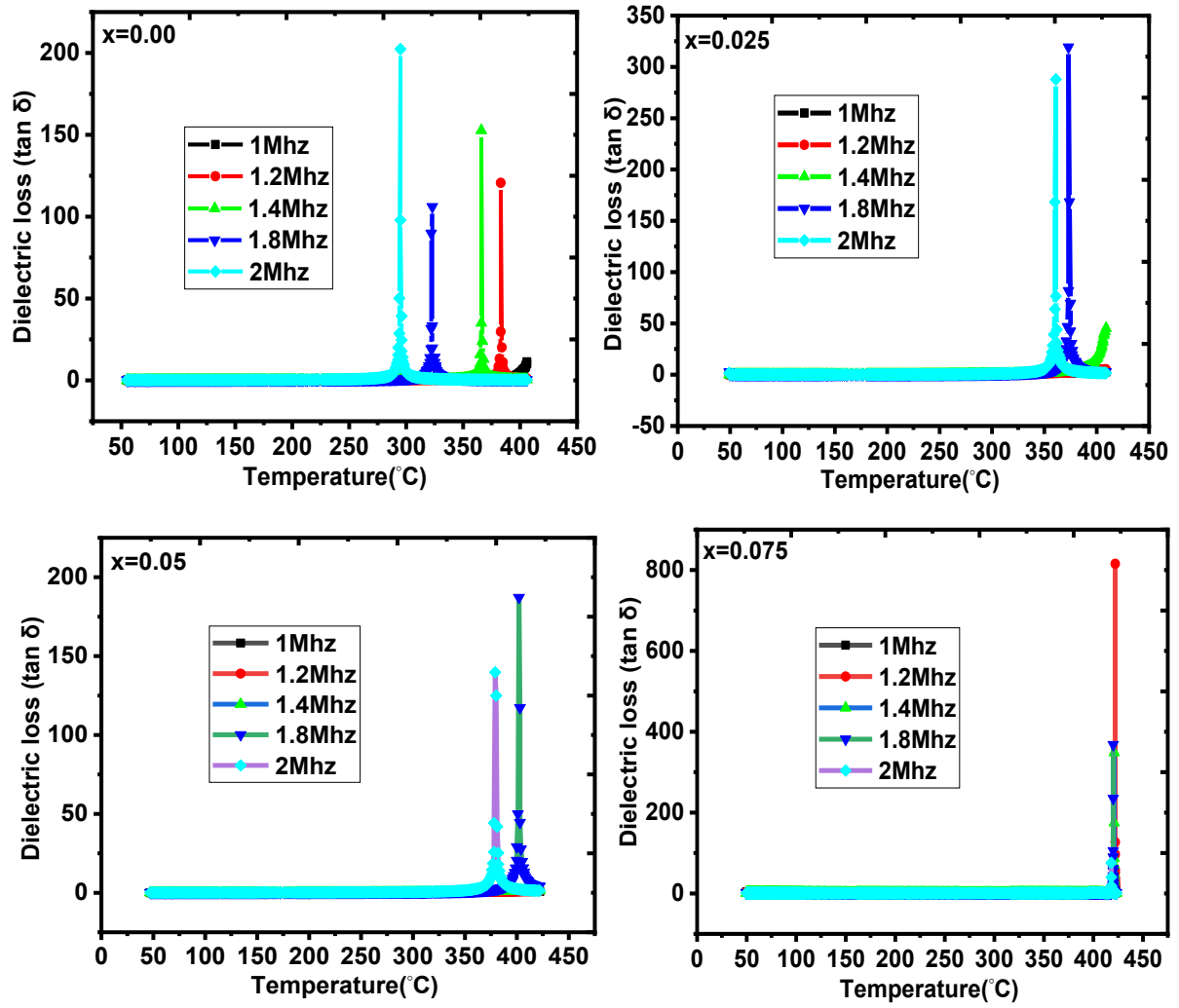


Figure 7: Variation of dielectric loss with temperature for PCxZT ceramics

Electrical Properties

Impedance analysis: Figure 8 shows the complex impedance spectra Z' (Z'') measured at different temperatures for PCxZT ceramics. Cole-Cole plots show a single semicircular arc whose diameter grows with increasing temperature. The single arc suggests that grain contributions are the main cause of the electrical response. Conduction activities within the grains are therefore fundamentally connected to the electrical phenomena seen throughout the whole temperature range under investigation. The radius of the semi-circular arc decreases with increasing temperature for $x=0.00$, $x=0.025$, and $x=0.05$, and increases for $x=0.075$. An upward trend in radius suggests positive thermal resistivity coefficient (PTCR) behavior, whereas a decrease in radius suggests negative thermal resistivity coefficient (NTCR) behavior in the ceramics[38], [39], [40]. Additionally, the center of the arcs of these compounds lies on the x-axis, suggesting a Debye-type relaxation[41][42].

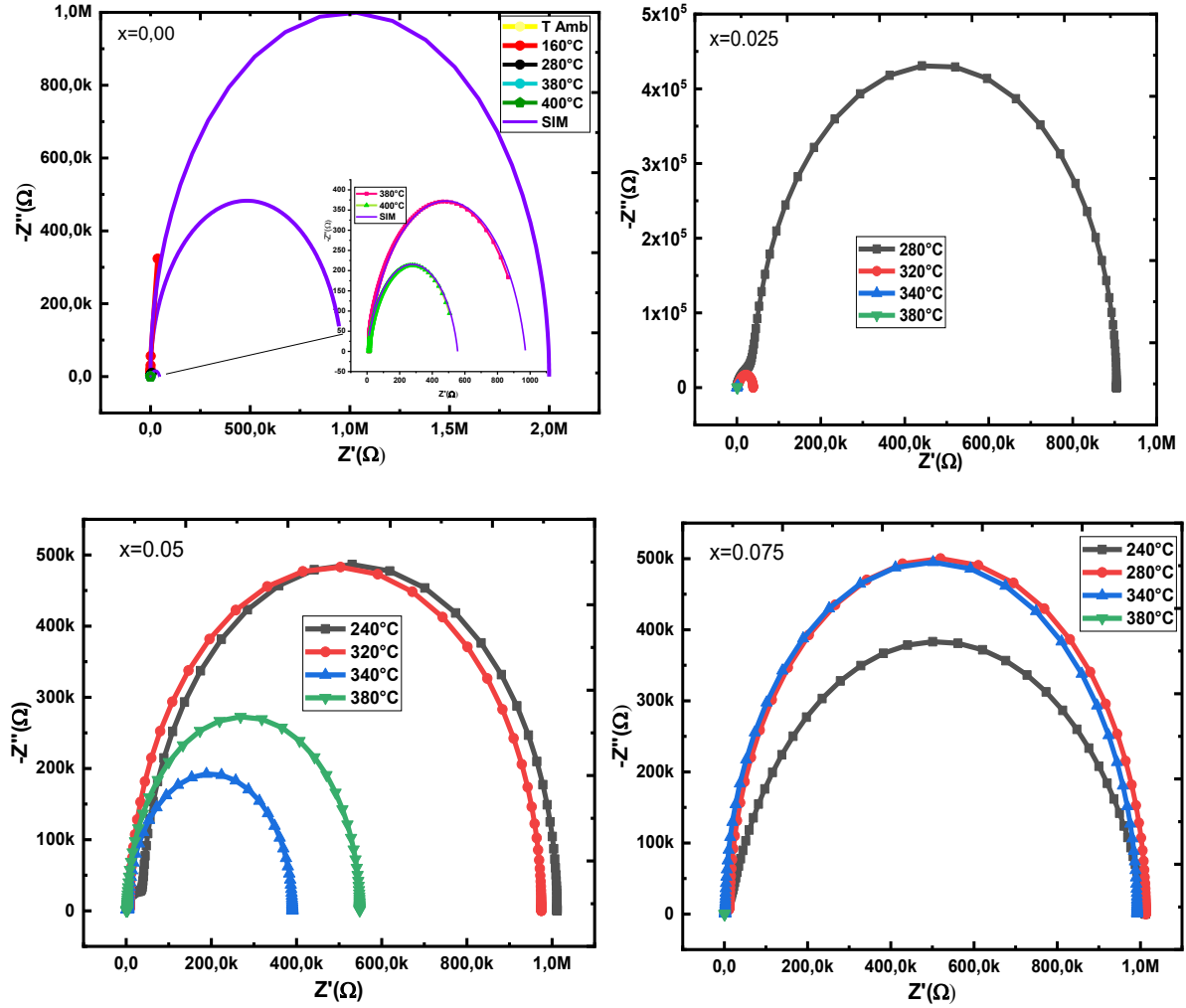


Figure 8 :Cole-Cole $Z''(Z')$ diagram for PCxZT ceramics

Activation energy

Figure 9 illustrates how PC_xZT ceramics' conductivity varies with the inverse of temperature. The temperature function's properties indicate that electrical conduction in the material is a temperature-activated process. Since the dependence of $\log \sigma$ at 100 kHz on $10^3/T$ is linear, we can calculate the activation energy (E_a) for PC_xZT ceramics with various Cu contents using the Arrhenius relationship below:

$$\sigma_{ac} = \sigma_0 \exp(-E_a/K_B T)$$

σ_0 is the pre-exponential factor, T is the material's temperature, K_B is Boltzmann's constant, and E_a is the activation energy, which can be calculated using the following procedure to trace the $\log \sigma_{ac}$ vs $10^3/T$ and estimate the height corresponding to the conductivity curve using the following formula :

$$E_a = (2.303 * 1000 * m. K_B)/e$$

Alternatively, e is the electron's charge, and m is the slope value.

The activation energy values for PCxZT ceramics are plotted against Cu concentrations in Table 3. It is apparent that the activation energy increases with increasing Cu content. These samples

have low activation energies, which could be a result of carriers bouncing between disordered localized states[32]. Oxygen vacancies are considered as moving carriers in perovskite-type ferroelectric materials, and their ionization produces conducting electrons that can be readily thermally activated[23], [43]. The information above renders it abundantly evident that oxygen vacancies are the cause of charge carrier conduction at high temperatures[44]. The Kröger-Vink reaction is accompanied by charge compensation, and oxygen vacancies due to oxygen loss are typically produced during sintering, which causes the increase in conductivity with temperature[45]: They belong to the "n" type because $O_{0x} \rightarrow 1/2O_2 + V_{0x}$ may leave behind free electrons.

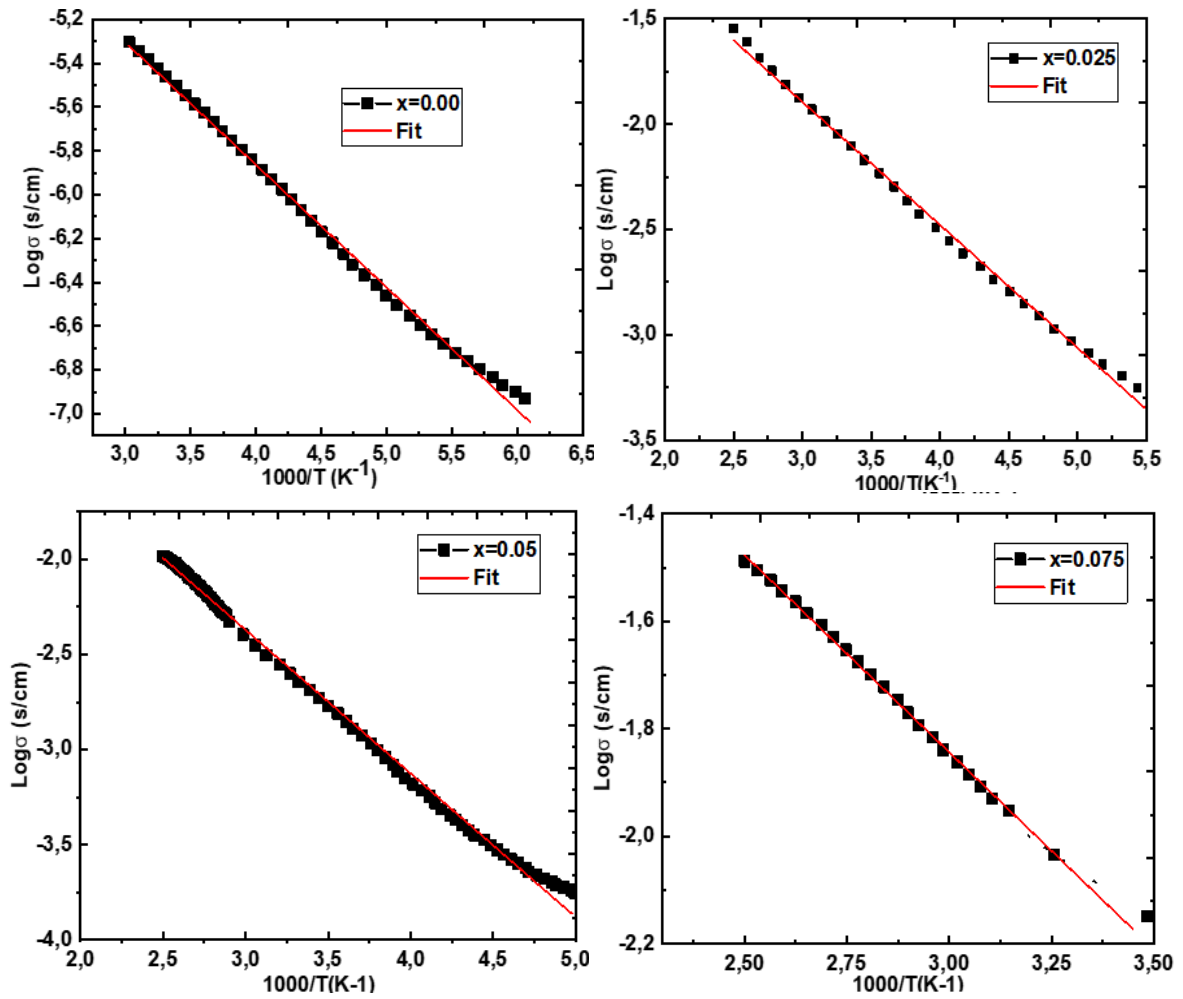


Figure 9: Activation energy (E_a) of PCxZT ceramics obtained by fitting the Arrhenius equation

Table 3: The change in activation energy (E_a) for PCxZT ceramics at 100 kHz

Values of x	Activation energy
x=0.00	0.11
x= 0.025	0.11
x= 0.05	0.149
x= 0.075	0.145

AC conductivity studies

All samples were analyzed for AC conductivity (σ_{ac}) to examine their dielectric properties. The following equation was used to calculate AC conductivity from the dielectric constant and loss factor.

$$\sigma_{ac}(\omega) = \omega \epsilon_0 \epsilon_r \tan \delta = 2\pi f \epsilon_0 \epsilon_r \tan \delta$$

in which ω_0 is the angular frequency, ϵ_r is the dielectric constant, $\epsilon_0 = 8.845 \times 10^{-12}$ F/m is the permittivity of free space, $\tan \delta$ is the dielectric loss, and $\sigma_{ac}(\omega)$ is the a.c. conductivity as a function of frequency. The DC conductivity variation of PCxZT ceramics as a function of frequency can be seen in Figure 10. As the image shows, conductivity increases steadily with frequency, followed by a rapid exponential rise. However, this growing effect happens significantly more quickly at all temperatures when using high-frequency data. Strong energy barriers at low frequencies could also be responsible for the rapid increase in conductivity at all temperatures, which corresponds to the drop in the dielectric constant[46]. An increase in frequency, however, corresponds to an increase in conductivity, as a greater number of lightly barrier charge carriers can respond easily to the applied frequency[47]. By comparing the graphs, the conductivity of PCxZT compounds increases as the Cu content increases. This increase can be explained by the difference between the radii of the Cu and Pb atoms in the PCxZT crystal lattices, which reduces the (resistive) barrier property[48][49]. In addition, it is also clear that the conductivity increases with increasing temperature, which suggests the negative temperature resistance coefficient (NTCR) behavior [50].

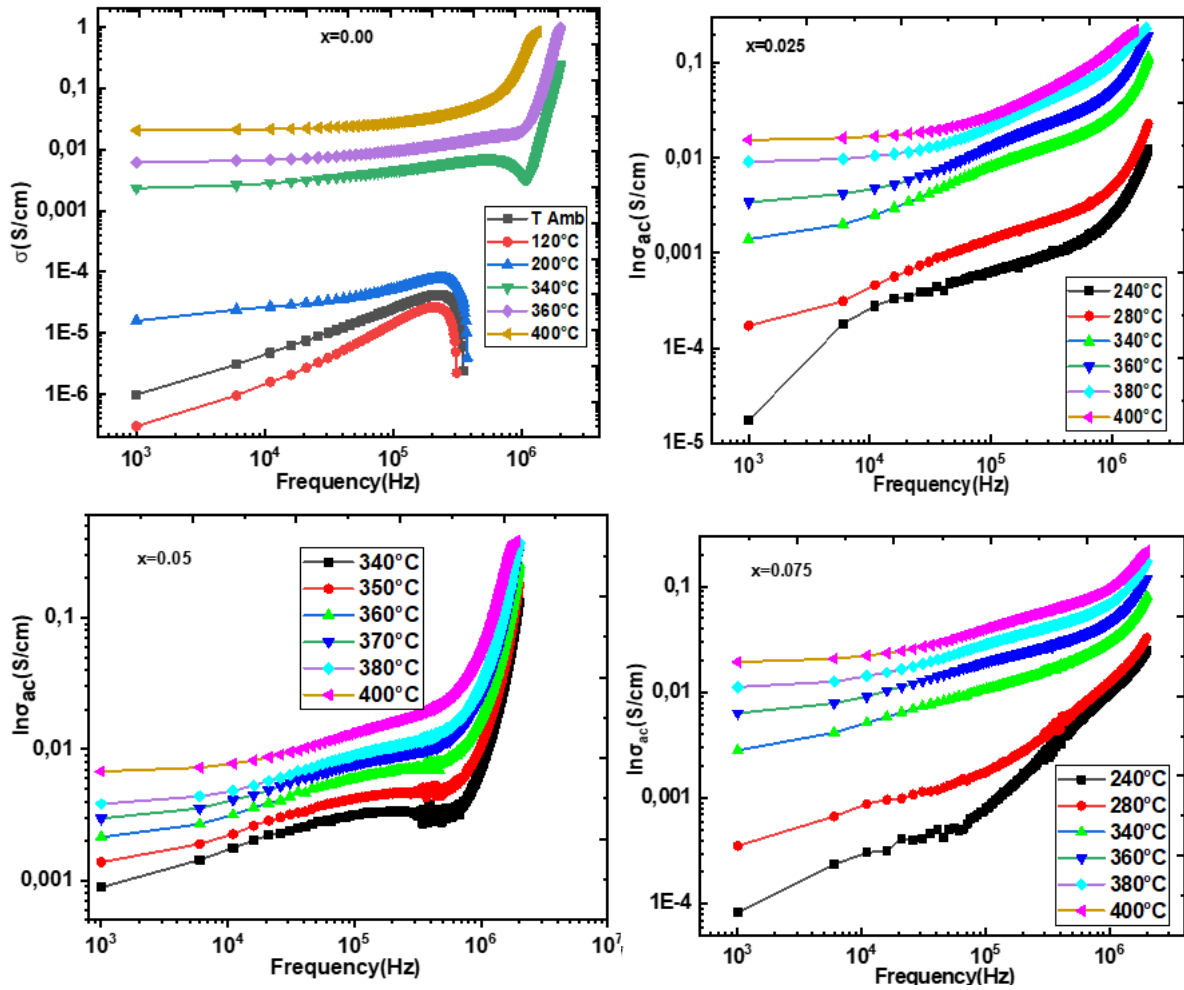


Figure 10: Conductivity versus frequency at different temperatures for PCxZT ceramics

Conclusion

PCxZT ceramics with $x = 0.00, 0.025, 0.05$, and 0.075 were prepared through the sol-gel route. X-ray diffraction confirms a perovskite structure combining rhombohedral and tetragonal phases. Crystallite size decreases progressively with increasing copper content. Microstructural observations near the morphotropic phase boundary show dense grains with irregular shapes. On the electrical side, dielectric measurements reveal a resonance phenomenon at high frequencies across the series. Impedance spectroscopy points to Debye-type relaxation. The activation energy rises with increasing Cu content, which likely reflects a change in the dominant conduction mechanism. Finally, electrical conductivity shifts toward a frequency-independent region as temperature increases, and this conductivity is enhanced overall with higher copper content.

Funding Declaration

The authors declare that they have no financial conflicts of interest that could influence this work.

References

- [1] L. Amarande, C. Miclea, M. Cioangher, M. N. Grecu, and I. Pasuk, "Effects of vanadium doping on sintering conditions and functional properties of Nb-Li co-doped PZT ceramics. Comments on Li location," *J. Alloys Compd.*, vol. 685, pp. 159–166, 2016, doi: 10.1016/j.jallcom.2016.05.266.
- [2] D. S. Seregin, M. Gerelt-od, K. A. Vorotilov, and M. R. Baklanov, "Interplay of Porosity, Defects, and Europium Doping in PZT Thin Films : Impact on Ferroelectric and Luminescent Behavior," 2026, doi: 10.1111/jace.71171.
- [3] C. Yan, X. Liu, H. Sun, H. Sui, and Y. Wang, "Enhanced ferroelectric and dielectric behaviors of PZT/BFO heterostructure via compositional development," *J. Mater. Sci. Mater. Electron.*, vol. 32, no. 7, pp. 8185–8194, 2021, doi: 10.1007/s10854-020-05024-9.
- [4] M. Khariief Amel, "Synthèse, caractérisations et étude structurale des céramiques PZT de type pérovskite $\text{Pb}_{1-x}\text{La}_x\text{Ca}_x[(\text{Zr}_Y\text{Ti}_{1-Y})_{0.75}(\text{Sb})_{0.25}]\text{O}_3$," Mémoire de Maîtrise, p. 101, 2012.
- [5] M. Siddiqui, J. J. Mohamed, and Z. A. Ahmad, "Structural, piezoelectric, and dielectric properties of PZT-based ceramics without excess lead oxide," *J. Aust. Ceram. Soc.*, vol. 56, no. 2, pp. 371–377, 2020, doi: 10.1007/s41779-019-00337-3.
- [6] R. Ranjan, R. Kumar, N. Kumar, B. Behera, and R. N. P. Choudhary, "Impedance and electric modulus analysis of Sm-modified $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})_{1-x/4}\text{O}_3$ ceramics," *J. Alloys Compd.*, no. 22, pp. 6388–6394, 2011, doi: 10.1016/j.jallcom.2011.03.003.
- [7] E. Pakizeh, "Optical response and structural properties of Fe-doped $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ nanopowders," *J. Mater. Sci. Mater. Electron.*, vol. 31, no. 6, pp. 4872–4881, 2020, doi: 10.1007/s10854-020-03050-1.
- [8] W. Jin *et al.*, "High-performance piezoelectric energy harvesting of vertically aligned $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ nanorod arrays," *RSC Adv.*, vol. 8, no. 14, pp. 7422–7427, 2018, doi: 10.1039/c7ra13506h.
- [9] C. P. Fernández, F. L. Zabotto, D. Garcia, and R. H. G. A. Kiminami, "In situ sol-gel co-synthesis at as low hydrolysis rate and microwave sintering of PZT/ Fe_2CoO_4 magnetoelectric composite ceramics," *Ceram. Int.*, vol. 43, no. 8, pp. 5925–5933, 2017, doi: 10.1016/j.ceramint.2017.01.100.
- [10] M. R. Mohammadi, S. A. Tabei, A. Nemati, D. Eder, and T. Pradeep, "Synthesis and crystallization of lead-zirconium-titanate (PZT) nanotubes at low temperature using carbon nanotubes (CNTs) as sacrificial templates," *Adv. Powder Technol.*, vol. 23, no. 5, pp. 647–654, 2012, doi: 10.1016/j.apt.2011.08.001.
- [11] D. Das, "Electromechanical response of textured ferroelectric PZT thin film stacks," University of Illinois at Urbana-Champaign, 2017.
- [12] M. Deluca *et al.*, "Raman spectroscopic study of phase transitions in undoped morphotropic $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$," *J. Raman Spectrosc.*, vol. 42, no. 3, pp. 488–495, 2011, doi: 10.1002/jrs.2714.
- [13] B. Noheda, J. Gonzalo, L. Cross, R. Guo, and S. Park, "Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 61, no. 13, pp. 8687–8695, 2000, doi: 10.1103/PhysRevB.61.8687.
- [14] W. Dmowski, "Structure of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}$ near the morphotropic phase boundary," vol. 33, no. 1, pp. 33–44, 2003, doi: 10.1063/1.1399687.
- [15] N. Zhang *et al.*, "The missing boundary in the phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$," no. May, pp. 1–9, 2014, doi: 10.1038/ncomms6231.
- [16] G. H. Khorrami, A. Khorsand Zak, A. Kompany, and R. Yousefi, "Optical and structural properties of X-doped (X = Mn, Mg, and Zn) PZT nanoparticles by Kramers-Kronig and size strain plot methods," *Ceram. Int.*, vol. 38, no. 7, pp. 5683–5690, 2012, doi: 10.1016/j.ceramint.2012.04.012.
- [17] F. Gheorghiu, R. Apetrei, M. Dobromir, A. Ianculescu, D. Luca, and L. Mitoseriu, "Investigation of Co-doped PZT films deposited by rf-magnetron sputtering," *Process. Appl. Ceram.*, vol. 8, no. 3, pp. 113–

120, 2014, doi: 10.2298/PAC1403113G.

- [18] A. Malika, G. Najwa, F. Z. Ahjyaje, L. Taj-Dine, and A. Farid, "Resonance Phenomenon and Structural Properties of Fe-Substituted PZT Ceramics Prepared by the Sol-Gel Method," *Iran. J. Mater. Sci. Eng.*, vol. 20, no. 1, pp. 1–14, 2023, doi: 10.22068/ijmse.2938.
- [19] N. Kumari *et al.*, *Multifunctional behavior of acceptor-cation substitution at higher doping concentration in PZT ceramics*, vol. 45, no. 10. 2019. doi: 10.1016/j.ceramint.2019.03.138.
- [20] P. P. Sukul, H. Swart, and K. Kumar, "Boltzmann relation reliability in optical temperature sensing based on upconversion studies of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped PZT ceramics," *Luminescence*, vol. 38, no. 7, pp. 1221–1229, 2023, doi: 10.1002/bio.4354.
- [21] B. Cherdhirunkorn, S. Surakulananta, J. Tangsritrakul, D. Hall, and S. Intarasiri, "The effect of nitrogen ion implantation on the physical and dielectric properties of cobalt-doped PZT ceramics," *Results Phys.*, vol. 16, no. August 2019, p. 102851, 2020, doi: 10.1016/j.rinp.2019.102851.
- [22] J. A. S. Caceres, C. A. C. Passos, J. V. S. Chagas, R. C. Barbieri, and R. T. Corteletti, "Study of structural and electric properties of the PZT 52/48 doped with Er^{+3} ," *Mater. Res.*, vol. 22, no. 5, 2019, doi: 10.1590/1980-5373-MR-2019-0123.
- [23] M. Prabu, I. B. Shameem Banu, S. Gobalakrishnan, and P. K. Praseetha, "Structural studies and electrical properties of PZT (52/48) electroceramics synthesized by sol–gel route," *J. Mater. Sci. Mater. Electron.*, vol. 27, no. 5, pp. 5351–5356, 2016, doi: 10.1007/s10854-016-4434-4.
- [24] M. Ahabboud, M. Amarass, Z. A. F. F. Abdi, and T. Lamcharfi, "Structural and dielectric properties of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-3x/4}\text{Fe}_x\text{O}_3$ ceramics at $0 \leq x \leq 0.20$ prepared by sol-gel method," *IOP Conf. Ser. Mater. Sci. Eng.*, pp. 1–3, 2021, doi: 10.1088/1757-899X/1160/1/012001.
- [25] M. Ahabboud, T. Lamcharfi, F. Abdi, N. Hadi, F. Z. Ajyaje, and M. Haddad, "Effect of Cu Doping on Structural and Dielectric Properties of $\text{Pb}_{1-x}\text{Cu}_x(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PCx ZT) ($0 \leq x \leq 0.2$) Ceramics Prepared by Sol-Gel Method M.," *Asian J. Chem.*, vol. 30, no. 18, pp. 2424–2430, 2018.
- [26] M. V. Ramana, M. P. Reddy, N. R. Reddy, K. V. S. Kumar, V. R. K. Murthy, and B. S. Murty, "Nanocrystalline $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ ferroelectric ceramics: Mechanical and electrical properties," *J. Nanomater.*, vol. 2010, no. May, pp. 0–8, 2010, doi: 10.1155/2010/783043.
- [27] C. A. Oliveira, E. Longo, J. A. Varela, and M. A. Zaghete, "Synthesis and characterization of lead zirconate titanate (PZT) obtained by two chemical methods," *Ceram. Int.*, vol. 40, no. 1 PART B, pp. 1717–1722, 2014, doi: 10.1016/j.ceramint.2013.07.068.
- [28] R. Ranjan, R. Kumar, B. Behera, and R. N. P. Choudhary, "Effect of Sm on structural, dielectric and conductivity properties of PZT ceramics," *Mater. Chem. Phys.*, vol. 115, no. 1, pp. 473–477, 2009, doi: 10.1016/j.matchemphys.2009.01.017.
- [29] E. Buixaderas, C. Kadlec, and P. Vanč, "Far infrared and Raman response in tetragonal $\text{PZT} \sim \text{b}$, Hana Uršič," vol. 4, pp. 219–224, 2015.
- [30] M. Deluca *et al.*, "Raman spectroscopic study of phase transitions in undoped morphotropic $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$," vol. 2010, no. April 2010, pp. 488–495, 2011, doi: 10.1002/jrs.2714.
- [31] E. Buixaderas, M. Berta, L. Kozielski, and I. Gregora, "Phase Transitions : A Multinational Raman spectroscopy of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ graded ceramics around the morphotropic phase boundary," *Phase Transitions*, no. July 2013, pp. 37–41, doi: 10.1080/01411594.2011.552049.
- [32] H. Li, J. Liu, H. Yu, and S. Zhang, "Relaxor behavior and Raman spectra of CuO -doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 ferroelectric ceramics," *J. Adv. Ceram.*, vol. 3, no. 3, pp. 177–183, 2014, doi: 10.1007/s40145-014-0106-0.
- [33] L. E. Fuentes-Cobas, J. A. Matutes-Aquino, M. E. Botello-Zubiate, A. González-Vázquez, M. E. Fuentes-Montero, and D. Chateigner, "Advances in Magnetoelectric Materials and Their Application," *Handb. Magn. Mater.*, vol. 24, no. January, pp. 237–322, 2015, doi: 10.1016/bs.hmm.2015.10.001.
- [34] M. S. Amer, *Raman Spectroscopy for Soft Matter Applications*, QC463.P5A4. United States of America, 2008. doi: 10.1002/9780470475997.

- [35] D. K. Pradhan, R. N. P. Chowdhury, and T. K. Nath, "Magnetoelectric properties of $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3\text{--Ni}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4$ multiferroic nanocomposites," *Appl. Nanosci.*, vol. 2, no. 3, pp. 261–273, 2012, doi: 10.1007/s13204-012-0103-y.
- [36] M. Ahabboud, N. Gouitaa, F. Abdi, and T. D. Lamcharfi, "Impedance Spectroscopy and Study of Electrical Properties of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{1-x}\text{Fe}_x\text{O}_{3-x}$ ($0 \leq x \leq 0.20$) Ceramics," *Mater. Sci. Forum*, vol. 1096, pp. 37–48, 2023, doi: 10.4028/p-0Ycat0.
- [37] S. H. Jo, S. P. Nam, S. G. Lee, S. H. Lee, Y. H. Lee, and Y. G. Kim, "Fabrication and electrical properties of PZT/BFO multilayer thin films," *Trans. Electr. Electron. Mater.*, vol. 12, no. 5, pp. 193–196, 2011, doi: 10.4313/TEEM.2011.12.5.193.
- [38] P. Lorena, *Multifunctional Polycrystalline Ferroelectric Materials*, vol. 1. 2015.
- [39] S. Hirano and A. Kishimoto, "Role of the interface in the temperature dependence of the resistivity of conductive composite thin films," *Japanese J. Appl. Physics, Part 1 Regul. Pap. Short Notes Rev. Pap.*, vol. 39, no. 3 A, pp. 1193–1199, 2000, doi: 10.1143/jjap.39.1193.
- [40] S. Manzoor, S. Husain, A. Somvanshi, and M. Fatema, "Investigation of relaxation phenomenon in lanthanum orthoferrite extracted through complex impedance and electric modulus spectroscopy," *J. Appl. Phys.*, vol. 128, no. 6, 2020, doi: 10.1063/5.0013245.
- [41] T. J. Ikyumbur, F. Gbaorun, and S. A. Ochi, "The Dielectric Study of Ethylene Glycol as a Coolant Using Davidson- Cole Relaxation Model," *Curr. J. Appl. Sci. Technol.*, vol. 32, no. 5, pp. 1–7, 2019, doi: 10.9734/cjast/2019/38947.
- [42] J. Manceau, "Etude du phénomène de relaxation diélectrique dans les capacités Métal-Isolant-Métal .," Joseph Fourier, 2008.
- [43] Z. Zhu, N. Zheng, G. Li, and Q. Yin, "Dielectric and electrical conductivity properties of PMS-PZT ceramics," *J. Am. Ceram. Soc.*, vol. 89, no. 2, pp. 717–719, 2006, doi: 10.1111/j.1551-2916.2005.00750.x.
- [44] C. C. Wang *et al.*, "Oxygen-vacancy-related dielectric relaxations in SrTiO_3 at high temperatures," *J. Appl. Phys.*, vol. 113, no. 9, pp. 1–10, 2013, doi: 10.1063/1.4794349.
- [45] J. Suchanicz, K. Kluczevska-Chmielarz, D. Sitko, and G. Ł. O. Jag, "Electrical transport in lead-free $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics J.," *J. Adv. Ceram.*, vol. 10, no. 1, pp. 152–165, 2021.
- [46] S. A. Raza, S. U. Awan, S. Hussain, S. A. Shah, A. M. Iqbal, and S. Khurshid Hasanain, "Structural, ferromagnetic, electrical, and dielectric relaxor properties of BaTiO_3 and CoFe_2O_4 bulk, nanoparticles, and nanocomposite materials for electronic devices," *J. Appl. Phys.*, vol. 128, no. 12, 2020, doi: 10.1063/1.5131467.
- [47] R. Gupta, S. Verma, D. Singh, K. Singh, and K. K. Bamzai, "Effect of Ni / Nb on structure, electrical and ferroelectric properties of," pp. 1–9, 2015.
- [48] B. Tiwari and R. N. P. Choudhary, "Study of impedance parameters of cerium modified lead zirconate titanate ceramics," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 17, no. 1, pp. 5–17, 2010, doi: 10.1109/TDEI.2010.5411996.
- [49] K. S. Cole and R. H. Cole, "Dispersion and absorption in dielectrics I. Alternating current characteristics," *J. Chem. Phys.*, vol. 9, no. 4, pp. 341–351, 1941, doi: 10.1063/1.1750906.
- [50] A. Feteira, "Negative temperature coefficient resistance (NTCR) ceramic thermistors: An industrial perspective," *J. Am. Ceram. Soc.*, vol. 92, no. 5, pp. 967–983, 2009, doi: 10.1111/j.1551-2916.2009.02990.x.