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The synthesis and characterization of alkaline niobate-based ceramic composites containing L-lysine Hydrochloride

Henry Ekene Mgbemere[1], **Viktoriya Semeykina**[2], **Chiedozie Valentine Oluigbo**[3*]

[1] Department of Metallurgical and Materials Engineering, University of Lagos, Akoka Lagos Nigeria
[2] Institute of Advanced Ceramics, Hamburg University of Technology, Denickestrasse 15, 21073, Hamburg, Germany.
[3] Department of Welding and Fabrication Engineering Technology, Federal Polytechnic Ilaro, Ogun State, Nigeria.

Orcid: H.E. Mgbemere (0000-0003-3887-7628), V. Semeykina (0000-0001-8175-3351), C. V. Oluigbo (0000-0002-8900-2883)

Abstract: Some lead-free piezoelectric ceramics are known to have high dielectric and piezoelectric properties but are limited by their brittle nature. A few amino acids have recently been reported to exhibit rather low dielectric and piezoelectric properties but have the advantage of being biocompatible and flexible. It would therefore be interesting to form a composite that will combine the inherent advantage of high dielectric properties from the ceramics and flexibility from the biomolecule. In this research, the properties of lead-free $(K_{0.45}Na_{0.51}Li_{0.04})(Nb_{0.85}Ta_{0.1}Sb_{0.05})O_3$ (KNNLST) ceramics and L-lysine hydrochloride (L-LHCl) have been combined to produce dielectric composites. The samples were produced by mixing the constituents from 0 wt.% to 100 wt.%, pelletising and heat-treating them. Bulk density, X-ray diffraction, scanning electron microscopy, and dielectric characterisation were techniques used to determine the density, phases, morphology, and dielectric properties of the produced composites. The results show an increasing bulk density value from 1.2 g/cm^3 for L-LHCl to 4.67 g/cm^3 for the KNNLST ceramics. The morphology of the composite shows very tiny grains when small amounts of the ceramics were introduced. The L-LHCl transforms from an amorphous phase to a crystalline phase having the orthorhombic-tetragonal structure with the introduction of the KNNLST ceramics. The dielectric constant values increased with increasing KNNLST ceramics content from 10 @1 kHz to 200 for the composite with 80 wt%. KNNLST content. The dielectric loss values decreased for L-LHCl from 0.9 @1 kHz to 0.2 @1kHz. The electrical conductivity values increased with increasing KNNLST ceramics content. The results show that the composites produced from these constituents may be suitable for dielectric applications.

Keywords: L-lysine hydrochloride, KNN ceramics, Composites, Synthesis, Dielectrics

1. Introduction

Poly L-lysine hydrochloride is a synthetic water-soluble polypeptide with properties similar to other lysine molecules. The crystal structure of amino acids is classified based on the system proposed by Gerbitz [1], where the hydrogen bonding arrangement of the head groups is used. The structure of the lysine molecule has been investigated with X-ray diffraction [2]. Amino acids are often used as ceramic templates, modifiers, and regulators. L-lysine monomer has a high affinity for water under normal atmospheric conditions [3]. It has a monoclinic symmetry with $P2_1$ space group and lattice parameters a = 9.54 Å, b = 5.14 Å, c = 17.06 Å, β = 97.78° (V= 828.9 Å^3). L-lysine monohydrochloride dihydrate (L-LMHCl) is grown using different techniques for non-linear optical applications [4]. Deionised water and its mixture with ethanol have been used to grow L-lysine monohydrochloride dihydrate (L-LMHCl) with lattice parameters: a = 5.8840 Å, b = 13.3359 Å, c = 7.5014 Å, and α = 89.92°, β = 97.63°, γ = 90.01° and

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Corresponding author:
Email: olu7wonders@yahoo.com

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V = 583.404 Å^3 for non-linear optical applications [5]. L-lysine hydrochloride and nano-crystallites of amorphous L-arginine hydrochloride substituted hydroxyapatite composite for dental applications have been investigated [6]. Using alkaline and acidic media, the effect of $CaCO_3$ substituted-hydroxyapatite, L-lysine, and L-arginine has been investigated [7]. Bonding was observed on the side chain of L-lysine HCl, while the hydroxyl groups of hydroxyapatites created an anionic form of L-lysine when the pH was ≤ 5. Composites from Potassium dihydrogen phosphate (KDP) crystals and L-lysine were grown, and the dielectric constant and loss values of the pure KDP crystals were better than those of the composite [8].

With different solvents, the structure of Poly-L-lysine has been studied [9]. Amino acids have recently been reported to exhibit dielectric and piezoelectric responses [10], which are, however, low, with a dielectric constant value of about 10 and piezoelectric constant values between 0.02 and 100 pC/N [11]. Ceramics like Lead zirconate titanate (PZT), $K_xNa_{1-x}(NbO_3)$ (KNN), and Barium titanate (BT) possess relatively high electrical responses. Their values are usually in orders of magnitude higher than those of amino acids. The challenge with piezoelectric ceramics generally is that they are usually very rigid and fail catastrophically in service most times. There have also been efforts to eliminate the use of lead-based piezoelectric ceramics because of their toxicity. KNN-based ceramics have been researched severally in the last couple of years, and they have been reported to exhibit relatively high dielectric and piezoelectric properties [12,13]. Composites typically act as a bridge to lessen the effect of monolithic materials like ceramics and amino acids in fabricating devices like sensors and actuators for electromechanical applications. Ceramics and amino acids tend to modulate the response of the resulting composite. The type, arrangement, crystal structure, and stress/strain application are some of the factors that determine the magnitude of these interactions. In this research, L-LHCl has been mixed with KNNLST ceramics to form a wide range of dielectric composites. The research aims to investigate how the beneficial properties of both L-LHCl and KNNLST ceramics can be combined to properties suitable for producing dielectric devices.

2. Materials and Method

2.1. Ceramics preparation

To prepare the KNNLST ceramics, raw powders of the following ceramics were used as procured: Na_2CO_3, Li_2CO_3, K_2CO_3, (99+%), Nb_2O_5, Ta_2O_5 (99.9%) (Chempur Feinchemikalien und Forschungs GmbH, Karlsruhe, Germany), and Sb_2O_3 (99.9%) (Alfa Aesar GmbH Kandel, Germany). The correct quantities of the individual powders were measured. The powders were then milled using an attritor mill operating at 500 rpm for 2 h, where zirconia balls (3 mm diameter) and ethanol were the milling media. After milling, the ethanol was separated from the powder using a solvent extractor, while the powder was calcined using a tube furnace. The furnace parameters are 3 °C/min heating rate to 850 °C, for 4 h holding time and 10 °C/min cooling rate. The powder was milled again using the same parameters to ensure small particle sizes.

2.2. Composite preparation

The composite was produced by weighing the required quantity of L-LHCl and then dissolving it in 10 ml of deionised water. The following compositions of the composite in weight percentage were made: 0, 20, 40, 50, 60, 80, and 100. The L-LHCl was then placed in a magnetic stirrer, and the temperature was gradually increased until it stabilised at 70 °C and maintained for 90 min to allow for complete dissolution. The ceramic powders are then slowly introduced to the solution and continuously stirred at 70 °C for 90 min until a slurry is formed. Ethanol was added to the solution to enable re-precipitation of the ceramic powder, and a centrifuge was used to decant the solvent from the composite solution. The resulting cake was allowed to dry. The powder was pressed using a uniaxial press operating at 10 kN for 30 s and a cold isostatic press at 500 MPa for 2 min. The samples were heat-treated at 150 °C for 48 h. Bloating of the sample was observed on the L-lysine hydrochloride.

2.3. Composite characterisation

The bulk density values of the samples were determined geometrically by measuring the dimensions and the mass. A minimum of 5 samples for each composition was used to determine the density value. The scanning electron microscope images were acquired using field emission scanning electron microscopy (SEM, Zeiss Supra VP 55, Jena, Germany). The samples were coated with silver paints at the sides to reduce the incidence of sample charging during the measurement. Enough vacuum was generated inside the sample chamber before the measurements were initiated. The images were acquired using the Secondary electron detection mode.

The phases in the samples were determined with an X-ray diffractometer (Bruker D8 Discover, USA) operating with Cu$k\alpha$ anode (λ = 1.5406 Å) at a voltage of 40 kV and 40 mA. The measurement was made from 10° to 60° using Grazing Incidence diffraction mode (GID) with a source fixed angle of 5°, a scanning speed of 3 s with an increment of 0.01°. The samples for electrical characterisation were coated with silver paints on both sides and poled in silicon oil at room temperature with electric fields between 1 – 2 kV/mm for 5 min, depending on the composition. The dielectric characterisation was carried out to determine the dielectric constant, dielectric loss, and conductivity by attaching metallic wires to both sides of the Ag-coated sample. The measurement was done at room temperature with an LCR meter (HP 4284, USA). Polarisation hysteresis measurements were attempted with a Sawyer-Tower circuit, but the samples' charging was too high to obtain a suitable measurement.

3. Results and Discussion

3.1. Density

The bulk density values of the L-LHCl-KNNLST composite are shown in ▶**Figure 1**. The density of L-LHCl is 1.2049±0.01 g/cm^3 and is 6% less than the density of 1.28 g/cm^3 [14]. As the content of ceramics increases, the density of the composite also increases gradually. The L-LHCl-KNNLST composites tend to be bloated through gas formation during fast heat treatment (especially L-LHCl 80-KNNLST-20), and so needed to be progressively heat-treated from 100 °C to 150 °C, and it affected the obtained density values. The density is enormously increased from 2.05±0.08 g/cm^3 for 60 wt.% to 3.415±0.077 g/cm^3 for 80 wt.%. This value represents 73 % of the density of the ceramics, which was calculated to be 4.67±0.07g/cm^3.

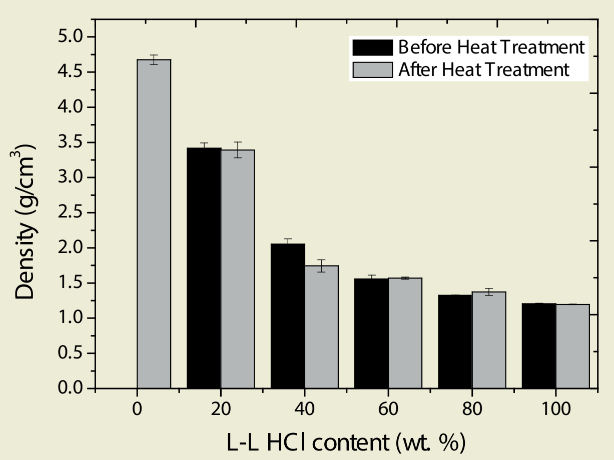

Figure 1. Bulk density values for L-lysine hydrochloride-KNNLST composite measured at room temperature.

3.2. Scanning Electron Microscopy

The scanning electron microscopy images for the L-lysine HCl-KNNLST composite are shown in ▶**Figure 2**. For the pure L-LHCl, a film is observed on the surface of the micrograph. A few tiny graphs could also be observed but there are little of no grain boundaries observed, corresponding to the obtained X-ray diffraction pattern. Microcracks and a few rod-like grains can be observed on the sample's surface, which is dense, containing few pores, and relatively rough. It is believed that the heat-treatment process led to some form of polymerization. The SEM images of L-lysine HCl mixed with water and ethanol have been reported to create bubbles [5]. Using Atomic Force Microscopy, Lysine HCl has been reported to have aggregation properties [15]. The introduction of 20 wt.% of KNNLST led to the formation of a crystalline phase. A lot of sub-micron-sized grains could be observed with few amorphous phases. Some grains exhibit the quasi-cubic morphology associated with KNN-based ceramics with few rod-like grains. The sample is relatively dense with uniformly distributed crystallites but contains little porosity. When the ceramics content increased to 40 wt.%, many cracks were observed, possibly due to differences in the expansion/contraction coefficient between the ceramic and the amino acid. The sample is crystalline with grains of different sizes and shapes. Most grains are in the sub-micron size range, and rod-like grains could be observed this time. There is good homogeneity in the distribution of the grains with densely packed grains and few porosities. Increasing the content of the ceramic to 60 wt.% increases the crystallinity of the sample with bi-modal grain size distribution. Some grains are in the sub-micron size range, while others are above 5 μm. The large grains appear to be somehow porous, with some signs of dissociation to form tiny grains. Cracks could also be observed on the surface. When the KNNLST content is 80 wt.%, the microstructure in the composite is remarkably different, showing clear crystallinity. The grains are plate-like with thickness in the nanometer size range, while the diameter of the grains is above 2 μm. There is homogeneity in the distribution of the grains in the composite. The composite is also relatively dense, with little porosity in the microstructure. A new microstructure different from those of L-LHCl and KNNLST was formed.

3.3. X-ray Diffraction

The X-ray diffraction patterns for the L-lysine HCl-KNNLST composite are shown in ▶**Figure 3**. The diffraction pattern for L-LHCl shows an amorphous structure with many broad, interconnected peaks. Lysine as an amino acid is crystalline [9,16], but the introduction of HCl led to the structure becoming almost amorphous. The broad peaks are observed throughout the whole range of the measurement, from 20° to 60°. The introduction of KNNLST ceramics led to a crystalline diffraction pattern. Sharp diffraction peaks with high intensities could be observed at 23°, 27° and 50°, respectively. Increasing the KNNLST content to 50 wt.% resulted in the coexistence of the KNNLST and L-LHCl patterns. When the quantity of KNNLST ceramics increased to 80 wt.%, the diffraction pattern was contributed mainly by the KNNLST ceramics. When only the KNNLST ceramics were present, the two-phase orthorhombic-tetragonal pattern associated with modified KNN ceramics was observed.

3.4. Dielectric properties

The dielectric properties graph for the L-LHCl-KNN-LST composite is shown in ▶**Figure 4**. As the content of KNNLST ceramics increases, the dielectric constant values also increase, possibly due to high polarization in the ceramics. As the frequency of measurement increases, the dielectric constant values are found to decrease. This is because, at lower frequencies, all the polarization mechanisms are present. Still, as the frequency increases, the natural frequency of bound charge is no longer equal to the frequency of the electric field. The irregularities usually observed at low frequencies are primarily due to electrode polarization [17]. L-LHCl has a dielectric constant value of 12 at 20 Hz, gradually decreasing to 7 at 1 MHz [5], introducing 20 wt.% KNNLST ceramics led to a slight decrease in the dielectric constant value from 14 at 20 Hz to 7 at 1 MHz. The dielectric constant values for 40 and 50 wt.% of KNNLST ceramics did not change significantly as the same trend was followed. A significant differ-

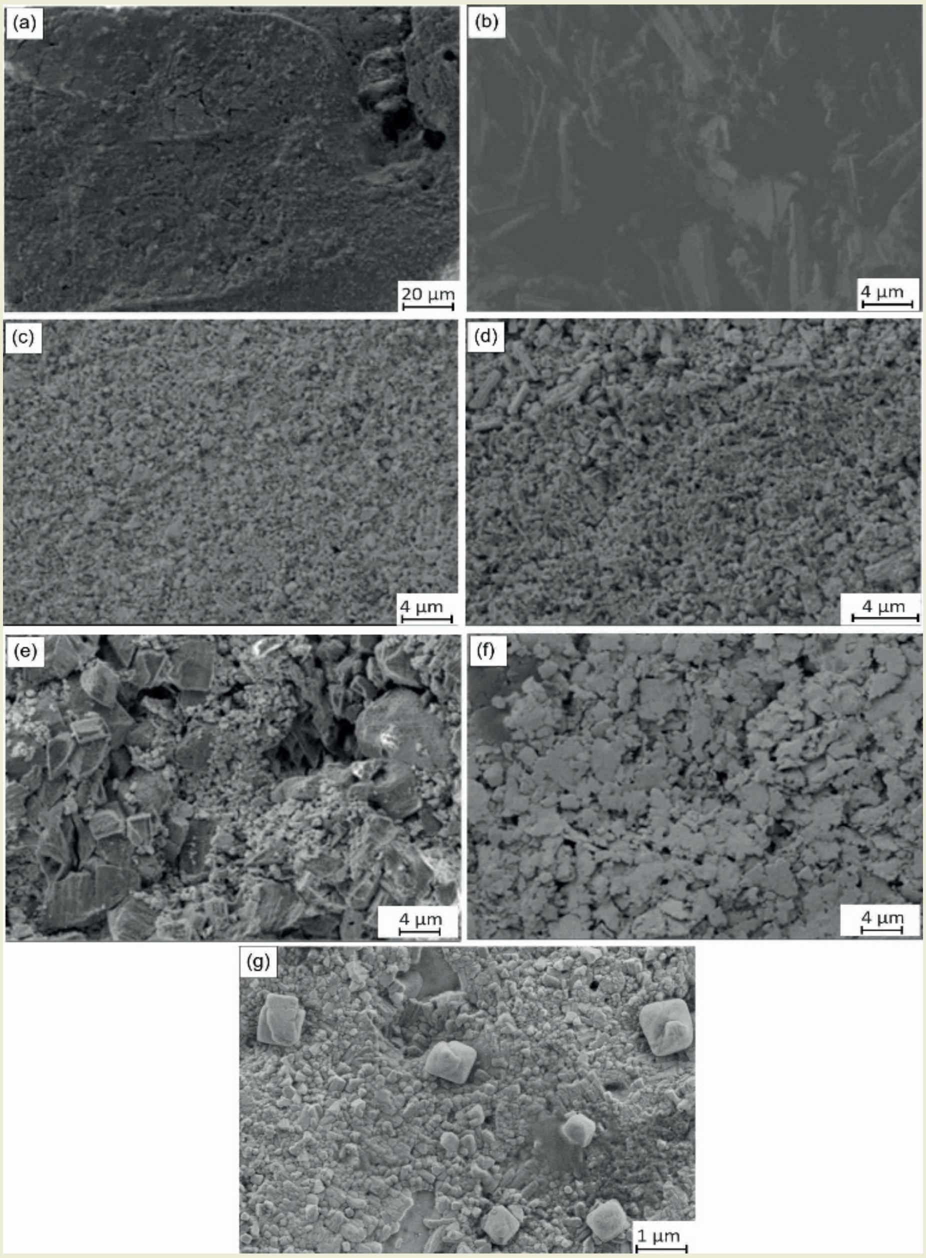

Figure 2. Scanning Electron Microscopy images for (a) L-LHCl (b) L-LHCl with water solution (c) L-LHCl 80-KNNLST 20 (d) L-LHCl 60-KNNLST 40 (e) L-LHCl 40-KNNLST 60 (f) L-LHCl 20-KNNLST 80 and (g) KNNLST ceramics.

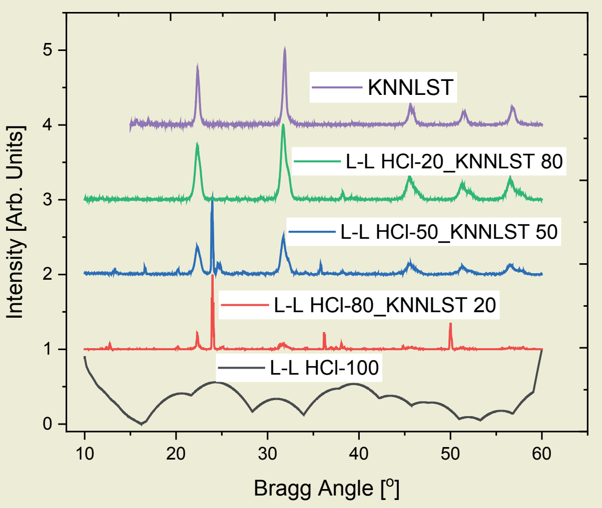

Figure 3. X-ray diffraction patterns for L-lysine HCl-KNNLST composite. The measurements were carried out at room temperature.

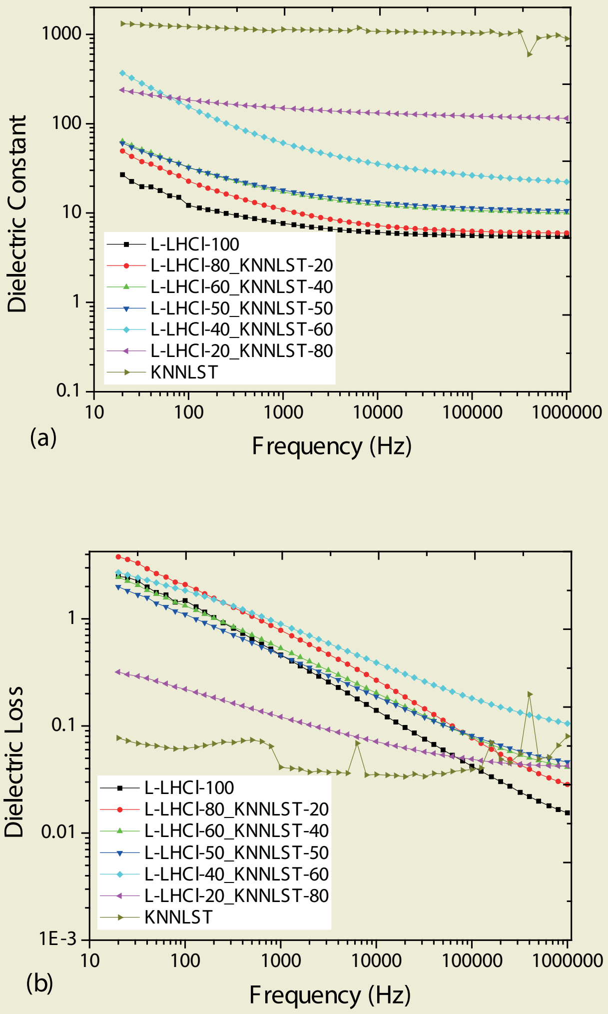

Figure 4. Log-log plots of (a) the dielectric constant and (b) the dielectric loss values for L-LHCl-KNNLST composites. The measurements were measured at room temperature.

ence was observed for 60 wt.% of KNNLST ceramics, where the dielectric constant at 20 Hz was 380 at 20 Hz and gradually reduced to 49 at 1 MHz. The composite containing 80 wt.% of KNNLST ceramics has the most stable dielectric constant value over the entire frequency range measured with a value of ~150. The dielectric constant value for the KNNLST ceramics is also stable, with a value of 1240 at 20 Hz, which gradually reduced to 934 at 1 MHz.

The dielectric loss values for the L-LHCl-KNNLST composite are shown in ▶**Figure 4b**. The dielectric loss values decreased with increasing frequency because, at low frequencies, dipole oscillation is present. Still, all the polarization mechanisms are absent at high frequencies, reducing the energy for dipole oscillation. The L-LHCl has a relatively high dielectric constant value of 3 at 20 Hz, steadily decreasing to 0.3 at 1 MHz. The dielectric loss values for the composite with ceramics content between 20 and 60 wt.% are similar to that of the amino acid—the composite containing 80 wt.% of KNNLST ceramic is more stable as the loss values varied between 0.3 and 0.08 from 20 Hz to 1 MHz. The dielectric loss value for KNNLST ceramics is stable over the frequency range measured between 0.05 and 0.1. The instability in the dielectric loss values is believed to result from resonance in the sample during the measurement.

3.5. AC Conductivity

The log-log plot of conductivity as a function of the measurement frequency is shown in ▶**Figure 5**. As the frequency for all the composites increased, the conductivity value increased. L-LHCl has the lowest conductivity value of all the samples measured. Its conductivity value at 20 Hz is 8 $*10^{-8}$ S/m and grows to 5 $*$ 10^{-6} S/m at 1 MHz. As the content of the KNNLST ceramics

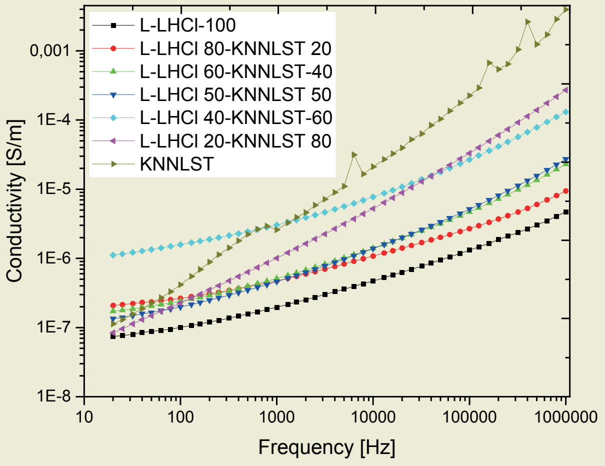

Figure 5. A log-log graph of conductivity as a function of frequency for L-LHCl-KNNLST composite.

in the composite increases, the conductivity values also increase. The conductivity value for KNNLST ceramics shows that at 20 Hz, the conductivity value is similar to that of other samples. Still, as the frequency rises to more than 1 kHz, the conductivity value increases more than any other sample. This is because there are more structural imperfections in ceramics, leading to the creation of more pathways for electrons to move.

4. Conclusion

The study examined the creation of a composite for dielectric devices by mixing L-Lysine HCl with KNNLST ceramics. The morphology of the L-LHCl was affected by the introduction of water as a solvent. The addition of ceramics resulted in the formation of new nanosized grains, and at high ceramics content, flake-like grains were obtained. The phases in the composites changed from amorphous for L-lysine HCl to two-phase tetragonal-orthorhombic for KNNLST ceramics. Increasing ceramics content increases the composite's dielectric constant value. The dielectric properties follow the same trend, decreasing with increasing frequency, while conductivity values increase with increasing frequency.

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Research Ethics

Ethical approval is not required.

Author contributions

Henry Ekene Mgbemere: Conceptualization, Formal analysis, Investigation, Writing original draft. **Viktoriya Semeykina:** Conceptualisation, Experiment and Formal analysis. **Chiedozie Valentine Oluigbo:** Formal analysis, Writing final draft, Review and Editing.

Conflicts of interest

The authors declare no conflicts of interest.

Research Funding

Not reported.

Data Availability

Not applicable.

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