Electrical and FTIR Studies on Kidney Stone

D. Aparna[1*], Jabbar Chyad Atiyah[2], Kaleem Ahmed Jaleeli[3], Majid Adil[4], N.V. Prasad[5]

[1,2,3,5]Department of Physics, Osmania University, Hyderabad, Telangana, India
[4]Department of Urology, Deccan Collage of Medical Sciences, Hyderabad, India

Corresponding Authors: aparna_dode@yahoo.com, nvp1969@rediffmail.com, Tel.: +919346939524

Abstract— Based on the geographical and habitual differences among the global population, it is reported that the majority of kidney stones are formed due to the disturbances occurred in metabolism. The kidney stone consists of collagen, calcium-oxalates, hydroxyapatite and many other phosphates. Moreover, water molecule and its traces are also present in kidney stone. Therefore, a kidney stone is considered to be ionic (or polar) nature, and has the capability of storing charges (dielectric). A large effort is being made, globally, in search of the origin of the behavior of kidney stone and, thereby it will be helpful for easy-removal, without surgery. In view of this, detailed impedance and FTIR studies were made on surgically removed urinary stone (kidney stone). The electrical results were compared with natural and human made promising materials namely bio-sample (banana peel) and electroceramics ($BaTiO_3$) for better understanding of the results.

Keywords— Kidney stone, impedance studies, dielectric relaxation, FTIR, Voigt fitting, bio-material

I. INTRODUCTION

Geographical and habitual differences observed among the global populations, it is presumed that the formation kidney stone can be controlled by understanding the metabolic disturbances or prime-reason for excretion of stone constituents [1, 2, 3, 4, 5, 6]. Clinical and a detailed epidemiological survey have revealed that risk factors such as dietary habits, climate condition, and familial history also help us to understand the true reason for kindly stone promoters [7, 8, 9, 10]. Therefore, a detailed spectral and electrical analysis of randomly chosen kidney stone provides information about the underlying cause, and it would be helpful in the surgical treatment.

In the early century (1904), a kidney stone was found in the pelvis of an ancient Egyptian- mummy lived in 4,800 BC. This was indeed quoted in many old medical reports of ancient Mesopotamia, India, China, Persia, Greece and Rome, and they have labeled as calculus disease [1]. However, after 1980, a new technique, named as extracorporeal shock-wave lithotripsy (breaking kidney stones via acoustical pulses), and thereafter this technique is being adapted globally.

Based on the literature [11, 12, 13, 14, 15, 16, 17, 18], it is found that the kidney stone consists of citrate. This acts as an inhibitor of stone formation and moreover it is originated from endogenous and exogenous sources. Here, it should be remembered that the diet is one of the main causative formation factor of all calcium-oxalate and uric-acid based kidney stones. Many researchers also pointed out that calcium-oxalate and uric-acid traces are generally found in patients of Asia and its southern adjoining areas [11, 12, 13].

It is a known fact that impedance analysis has been widely used to characterize the dielectric behavior of many ordered/disordered bio-materials (or electroceramics). A proper electrical study on kidney stone would be useful to understand the nucleation and its subsequent growth, and thereby one can arrest its formation.

II. RELATED WORK

The microscopic origin of this work is to explore the information on the asymmetric behavior of imaginary part of impedance respond function with the frequency, in a closed proximity. To extract more information about its intrinsic dielectric nature and ionic-relaxation phenomenon, impedance measurements were also performed on the nature-bio sample (musa acuminata colla) and $BaTiO_3$ (a promising electroceramic, which is being used in many sensors).

III. MATERIALS AND METHODS

The material used for this study was kidney stone (surgically recovered from the patient). Kidney stone was placed on the sterile wire-gauze to dry, and after that it transferred into a paper plastic bottle. Prior to this, the specimen was washed carefully with distilled deionized water and dried it over in a silica-gel for several days. In the present investigation the kidney stone was collected from New Life Hospital, Chatarghat, Hyderabad, India. Impedance measurements were made on kidneys stone,

banana peel (musa acuminata colla) and $BaTiO_3$ (human innovative sample) by using impedance analyzer HP 4192 A. Barium titanate ($BaTiO_3$) sample was prepared by solid-state reaction method, and a detailed part of this analysis would be discussed in due course. Prior to the measurements, all samples were coated with silver paste and heated under IR lamp. A schematic diagram of sample holder was already reported, elsewhere [19].

IV. RESULTS AND DISCUSSION

It has been reported in the literature that the intensity of XRD peaks were found to vary from kidney stone to kidney stone. The broad XRD peak was attributed to the poor crystalline nature of carbonate apatite phase [14]. However, it is reported that the overlapping of whewellite and hydroxylapatite phases made it difficult to identify the major component, and the significant amount of these two phases were observed in FTIR data [15, 16, 17, 18]. In view of this, impedance spectroscopy and dielectric analysis along with FTIR is studied in the present investigation.

Electrical impedance (Z) and phase angle (θ) were measured using impedance analyzer as a function of frequency (1 KHz to 1MHz) at room temperature. A change in real and imaginary part of impedance (Z' and Z") with frequency at room temperature is shown in Figure 1, for kidney stone (sample-A). From the plots, it is clearly observed that Z' values decreases gradually up to a certain frequency (100 KHz) and thereafter it attains to a constant value. In addition, a peak like behavior, observed for Z", is clearly indicating the relaxation process. This trend is generally observed in water-based (bio) dielectric materials as shown in the Figure 2 (banana peel, sample -B) [19].

A noteworthy aspect from the plots is that a sudden fall of real part of responds function (Z'$_{min}$) coincides to the maximum peak position of imaginary part of respond function (Z"$_{max}$). This type of behavior clearly indicates that the present material belongs to Debye type. The above mentioned behavior, observed at room temperature, is rarely reported in the literature. We have not observed any peak like behavior in case of promising electroceramics ($BaTiO_3$) sample, as shown in the Figure 3 (sample-C), due to high dielectric constant of the sample. A stereoscopic nature observed in sample -A and sample–B, reinforces our earlier conclusions that:

i). Bio-based materials are consist of strained hydrogen bonded network
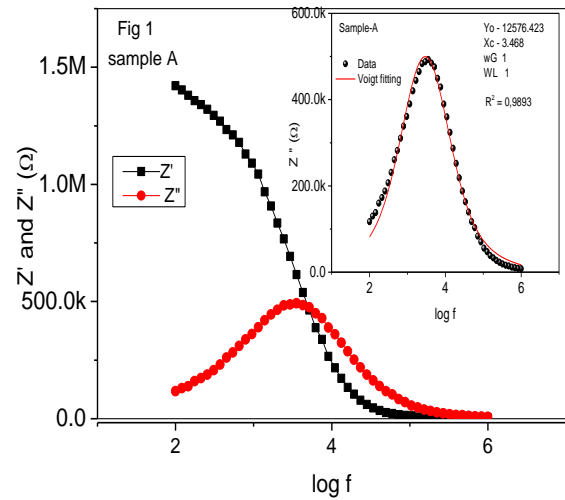ii). Bio-nature process allows a diffusion process of continuous cooperative interaction of neighboring network.

Figure 1. Z' and Z" vs log f for kidney stone (sample-A): Inset Fig Voigt fitting

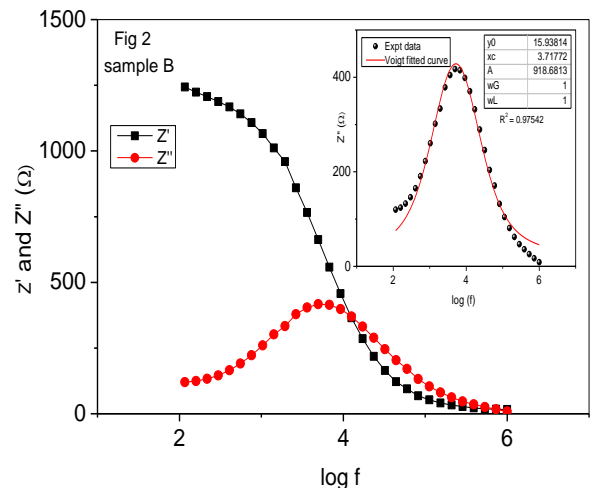

Figure 2 Z' and Z" vs. log f of Musa acuminata colla (sample B) [ref. 19]: Inset Fig. Voigt fitting

The dielectric relaxation of bio-samples (sample-A and -B) are ascribed to the hydrogen and non-hydrogen (carbon and other functional groups) bonded network and its statistical orientation-order. The sum of all dipoles (μ) is equal is to total vector sum of dipole (M):

$$M = \sum_{i=1}^{N} \mu_i \qquad (1)$$

For correlated and un-correlated dipoles, the requisite condition is:

$$\langle \frac{M^2}{N} \rangle = 1 \text{ (for uncorrelated system)} \qquad (2a)$$

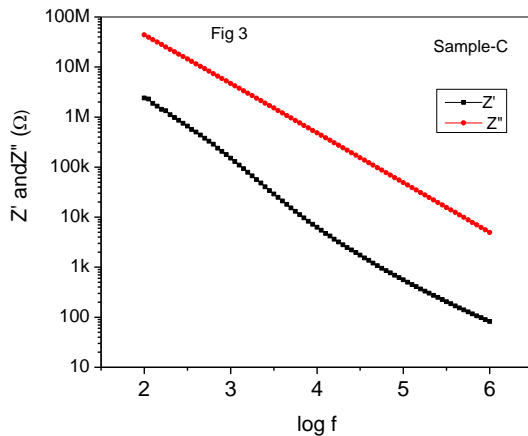And $\langle \frac{M^2}{N} \rangle > 1$ (for correlated) (2b)

Figure 3 Z' and Z" vs log f for $BaTiO_3$ electroceramic (sample C)

However, a more precise way to explain the effective potential (V eff) of the hydrogen and non-hydrogen bonded (HB and NHB) biomolecules is:

$$V_{eff\ (i,\ j)} < V_{HB} \qquad (3a)$$
$$V_{eff\ (i,\ j)} > V_{NHB} \qquad (3b)$$

The effective potential depends upon the interaction density (p) and potential (V), expressed as:

$$p(V) \quad \alpha \quad \int dx_j\ \delta[V - V_{eff}\ (x_i, x_j)]\ g(x_i x_j), \qquad (4)$$

Here the term $g\ (x_i, x_j)$ represents the correlative function, which is more or less depend on the Z" respond function, and its frequency dependent nature.

Aforementioned dielectric relaxations can be understood by means of traditional Cole-Cole plots and more adequate equation is as follows:

$$\frac{\varepsilon_0(\varepsilon(\omega) - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon(\omega)\ (\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)} = \int_0^\infty dt \exp(i\omega t)\ \frac{d\Gamma}{dt} \qquad (5)$$

Here ε_∞ and ε_0 represent high and low frequency dielectric constants respectively. The term $d\Gamma$ represents the exponential function which can be extracted by impedance spectroscopic plots (Z" vs. frequency). The following equation explains the autocorrelation of neighboring dipoles:

$$\Gamma = \langle P\ [\mu_i . \mu_j] \rangle \qquad (6)$$

It is a known fact that impedance respond functions of biomaterials are generally observed in the radio-frequency range. It also explains about the competitive interaction of neighboring dipoles that are present in the samples [20, 21]. This information can be extracted from the spectroscopic peak width and its shape [22]. The peak width of spectroscopic can be obtained by fitting the data either into Gaussian or Lorentzian equations. Here, the former equation explains about single relaxation and the latter explains about multiple relaxations phenomenon.

However, Voigt function explains the convolution of both Gaussian and Lorentzian (G(x) $\oplus$ L(x)) and moreover this function also gives a weightage to the numerical data. In the present investigation, the impedance data is fitted to the Voigt equation for the sample-A and sample-B respectively, and are depicted as inset in Figure 1 and Figure 2. The relaxation frequency for sample-A and sample-B were found to be 2947 Hz and 4954 Hz receptively. A proper care is taken while fitting the data in to Voigt equation, by keeping Gaussian and Lorentzian functions (W_G and W_L) as unity (See inset Figure 1 & 2 fitting data).

The complex permittivity (ε^*) can be expressed in terms of complex number by using the following relation:

$$\varepsilon^*\ (\omega) = \frac{1}{j\ \omega\ c_0\ z^*} \qquad (7)$$

Where Z^* and C_0 represents the complex impedance and geometrical capacitance of the sample. Since the shape of the sample is complex and it is difficult to measure geometrical ratio therefore, a change in the dielectric loss (tan δ) with frequency of kidney stone is shown in Figure 4. From the log-log plot it is clearly seen that the data is found to fit linearly, and the value is found to decreases with increasing the frequency. It clearly indicates the minimizing the space charge affects and brings the true values, as pointed out earlier [22]. Moreover the linear-nature is a clear evidence for a hoping mechanism [23, 24].
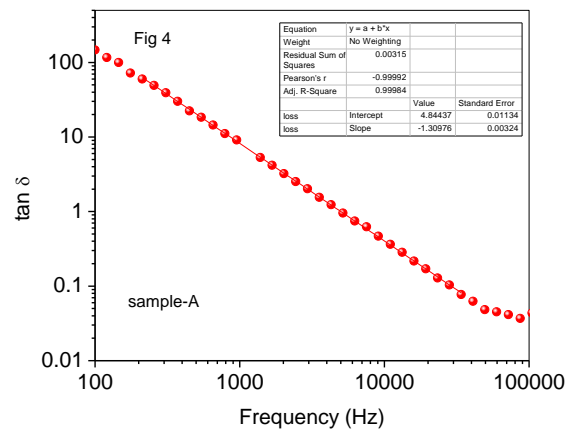

Figure 4 Variation of dielectric loss (tan δ) with frequency for sample-A

As mentioned earlier, the frequency dependent dielectric loss data can explain hoping conduction mechanism on account of the heterogeneous (existence of different ions) nature of kidney stone. The hopping mechanism can also be explained by the Universal relation $f \propto B\omega^n$. Here f denotes the response function (dielectric loss), which is related to $\varepsilon"/\varepsilon'$. In present investigation 'n' (exponent value) is found to be 0.9. This indicates that the sample is tuning to Debye type. Since the compounds have water traces, and during drying the kidney stone, water molecule may play role in the dielectric properties. In addition, due

       3

to the presence of the multivalent cities it may leads to defects such as vacancies. These defects (vacancies) certainly affect the conduction or dielectric mechanism. However, such charge transfer mechanism through hoping can be estimated by the value of 'n'. The 'n' value in the present investigation is found to be less than 1 (~0.9), indicates the hopping of ions. This indicates the system (kidney stone) have a high degree of disorder nature, and confirms the presence of ionic-dipoles and defects.

Complex impedance plot can explain us information about nature, as well as rate of charge transport process across the electrode interfaces. A detailed complex analysis provides information about Debye behavior and the dielectric relaxation phenomenon. A simple parallel R-C combination circuit is more adequate to represent the present complex electrical data. The variation of $Z^{'}$ versus Z" is shown in Figure 5, yields a semicircle, which indicates that the sample has parallel combinations of R and C network. Moreover, the inclined angle less than 9^{0} confirms the multiple relaxation (or non-Debye) and dipolar polarization phenomenon [23, 24]. This is attributed to the diffusion of defects that are generally present in the kidney stone. In other words, the displacement of heterovalent ions that are present in the sample starts playing a role in the conduction mechanism through interaction of neighboring sites, as mentioned earlier
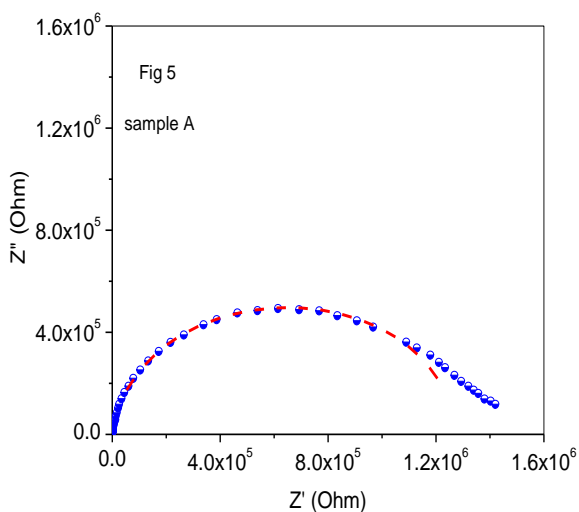
pressure of 5 tons /cm^{2}. The transmission spectrum was obtained on the disk sample of kidney stone in the range of 400 - 2000 cm^{-1}.

The infrared radiation refers broadly in to three regions of electromagnetic spectrum, which lies in the following regions.
a). The range from 12000 – 4000 cm^{-1} is called near infrared (NIR).
b). The range from 4000-400 cm^{-1} is called mid infrared (MIR).
c) The region below 400 cm^{-1} is the far infrared region (FIR).

Absorption observed in the infrared (IR) region generally results into the changes of vibrational as well as rotational states of the molecular system. It is a known phenomenon that the absorption-frequency and absorption-intensity depend on the vibrational frequency and transferred photon energy of the molecule. In addition, it explains about the change in the dipole moment and molecular vibrational states. In view of this, molecule absorbs infrared light only. In IR-spectroscopy, if IR radiation is passed through a sample a part of radiation is absorbed and the remaining transmitted through the sample. Thus the resulting IR-spectrum shows the molecular-absorption and molecular-transmission information of the sample. Since most materials interact with IR-light, Fourier transformation infrared (FTIR) analysis gives us qualitative as well as quantitative information of the sample.
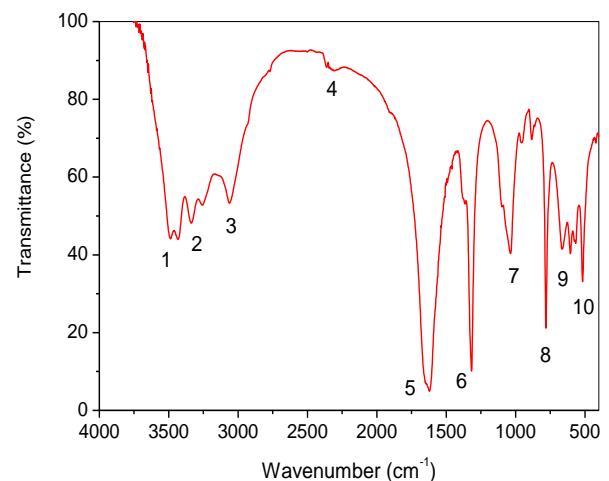

Figure 5 *Cole-Cole plot (Z'' vs. Z')*

Figure 6 FTIR on kidney stone

To understand the effect of environmental and etiological role on the growth of kidney stones, it is necessary to know the chemical constituents of the sample. The composition of stones varies from patient to patient and also with time. Moreover no systematic study on combined spectroscopic analysis on urinary stone is available in the literature. Therefore, in the present investigation, FTIR studies are carried out using BRUKER OPTICS, model TENSOR 27 instrument. The kidney stone was ground to fine powder and then mixed with KBr powder in the ratio of 0.002: 0.2 gm. The mixture-powder was then subjected to a constant

Fourier transformation infrared (FTIR) spectroscopy of the kidney stone, measured at room temperature, is given in the Figure 6. The sharp absorption peaks obtained from the present samples are at 3000 cm^{-1} and 3500 cm^{-1} and with another peak at 2250 cm^{-1}. The three bands marked as 1, 2 and 3 are attributed to symmetric as well as asymmetric stretching of OH-bands The sharp peaks observed at 1000 cm^{-1} and 1320 cm^{-1} (marked as 4 and 5 in the spectra) is attributed vibration modes of double and single bonds of carbon (C=O and C-O) [25 -27]. The peak appeared at 520

cm^{-1} (peak 9) is mainly due to O-C-O plane bending as pointed out in the literature [25-27]. The peaks clearly confirms that the kidney stone consists of calcium oxalate dehydrate substance. The broad band, marked as 4, is attributed to symmetric and asymmetric OH-stretching vibration. Generally a peak at 1450 cm^{-1} represents carbonate group. Based on this, a tentative conclusion is arrived that hydrogen bonded nature predominant over the carbons based bands. Since no peaks are observed in the range of 1450 cm^{-1} – 1410 cm^{-1} and at 712 cm^{-1} (bands observed at 8 and 9) confirms the same. The bands observed near 778 cm^{-1} indicates the presence of calcium oxalate traces [27].

The FTIR spectrum of the kidney stone resembles with the calcium oxalate monohydrate spectrum. The bands observed in the range 3500–3200 cm^{-1} is ascribed to the symmetric and asymmetric bond stretching of water molecule. The strong peaks and weak bands observed at 1620 cm^{-1} and 661 cm^{-1} is ascribed to the bending and wiggle modes of the water (H_2O) molecule.

In human urine, the concentration of oxalates affects the supersaturating state and creates a condition to grow the oxalate crystals and finally leads to oxalate-based kidney stones formation. An increase of oxalate promotion takes place from our diet and also helps the desired pH value (below 7). Urine is itself a complex solution; consist of calcium, magnesium, urea, oxalate, and other proteins. The mutual interactions of the micro-protein suspended complex solution certainly change the solubility of the constituents and allows to a stone-growth. Finally, the promoters and inhibitors in the urine influence an environment of kidney-stone formation. However, more research on this aspect is required for further interpreting the growth and its mechanism.

V. CONCLUSION AND FUTURE SCOPE

Frequency dependent impedance respond-function such as (Z") showed a broad peak and the full width at half maximum (FWHM) value was found to be more than 1.16. From this, one can conclude that the relaxations observed in the kidney stone are approximated Debye type. The dielectric relaxation is frequency-dependent nature, and therefore it is concluded that the kidney stone consists many cationic or defect vacancies. These defect vacancies form diploes with electron in turn leads to dielectric relaxation effects. The results are consistent with the complex Cole-Cole plot. From the double logarithmic plot (log tan δ vs. log frequency), it is clearly seen that the response function is linear nature and the exponent values is found to be 0.9. This is clearly confirms the hoping conduction mechanism, which plays a dominant role in the conduction process through the migration or exchange of electron with its neighboring sites. The most important and striking feature observed in the dielectric analysis is that an increasing trend of the dielectric loss at higher frequency gives an idea about how these materials behave with the applied alternating current at various frequencies.

Based on the intrinsic dielectric nature of the kidney stone, it is concluded that the electrical properties of the kidney stone could be related to their mechanical behavior due to the piezoelectric effect wherein this property could be used in extracorporeal shock wave lithotripsy. Therefore, one can speculate that breaking the kidney stone is the easier-process in the surgery. Moreover, the aggregation and adhesion of particles may help the growth of the kidney stones in vivo. In addition, a relative large data on many samples can also be helpful to understand the formation of urinary calculi in-vivo pathological conditions. A proper density function theory based on the different samples will help us to understand the inhibited mechanism. From this, one can arrest the growth from therapeutically.

VI. ACKNOWLEDGEMENTS

REFERENCES

[1] J M Soucie, R J Coates, W Mc Clellan, H. Austin, M. Thun, "Relation between geographic variability in kidney stones, prevalence and risk factors for stones" . *Am J Epidemiol*. vol. **143**: pp. 487 – 495, **1996.**

[2]. G. Maschio, N D Tessitor, A. Angelo A, et al. "Prevention of nephrolithiasis with low dose thiazide, amiloride and allopurinol". *Am. J Med*. Vol. **71**, pp 623-26, **1981**.

[3]. B. Dussol, Y. Berland, *"*Urinary kidney stone inhibitors: what is the news?" *Urol Int*. vol, **60:** pp 69-73, **1998.**

[4]. C. Paluszkiewicz, S. Jand, M. Galka, *"*Analysis of renal stones by FTIR spectroscopy". *Microchimica Acta*., vol. **94**, pp 45 – 48**, 1988**.

[5]. A Mayo Reference Services Publication. Kidney Stones and Stone Analysis. *Communique* vol. **26** (5), pp 1-6, **2001.**

[6] A R Michell, Urolithiasis - historical, comparative and pathophysiological aspects: A review. *J Roy Soc Med*, vol **82**, pp 669-72**, 1989**.

[7]. H Clegg and M Ware, Composition of kidney stones. *Br Med J*. vol **1**, pp: 1392 – 96, **1965.**

[8] F L Coe, Prevention of kidney stone. *Am J Med*, vol **71**, pp 514 – 16, **1981**.

[9] H G Tiselius, L H Smith, W G Robertson, B Finlayson et al. (eds). *Urolithiases: clinical and basic research. Plenum pub*, New York. pp **3944, 1980.**

[10] J H Parks, F L Coe FL, A Urinary calculi nephrolithiasis. *Kidney Int*. vol **30**, pp 85 – 90, **1986**.

[11] R. Nath, S.K. Thind, M.S.R. Murthy, H.S. Talwar, S. Farooqui, Molecular aspects of idiopathic urolithiasis. *Molecular Aspects of Medicine*, vol **7**, pp 171-176**, 1984**.

[12] B Baggio Genetic and dietary factors in idiopathic calcium nephrolithiasis: what do we have, what do we need? *J Nephrol*. Vol **12**, pp 371 – 374**, 1999.**

[13] K.K. Bamzai, S. Suri, V. Singh, Synthesis, characterization, thermal and dielectric properties of pure and cadmium doped calcium hydrogen phosphate, *Mat. Chem. and Phys*. Vol **135**, pp 158-167**, 2012**.

[14] Debottam Sinha, K.Anwar, K.Kumari, S.Jaishwal, S.MadeshwaranS.Keshari, D.Rajan Babu , Vidya. R,b, Arunai Nambiraj.N, "Studies on the Dielectric properties of Natural Urinary Stones*" Adv. Mat. Res*. Vol **584**: pp 484-488**, 2012**.

[15] J S Elliot, M E Rebiro, The urinary excretion of citric, hippuric, and Lactic Acid in normal adult and in patients with calcium oxalate urinary calculus diseases. *Invest Urol*. Vol **10**, pp 102 – 106**, 1972**.

[16] S G Welshman, M G McGeorn, Urinary citrate excretion in stones formers and in normal controls. *Br J Urol*.vol **48**: pp 7 – 11, **1978.**

[17] H G Tiselius, L H Smith, W G Robertson, B Finlayson et al. (eds). *Urolithiases: clinical and basic research.* Plenum pub, New York. Pp. **3944. 1980**.

[18] J H Parks, and F L Coe, A Urinary calculi nephrolithiasis. *Kidney Int.* vol **30**: pp 85 – 90, **1986.**

[19] Omprakash, N. V. Prasad, G. Prasad, V.G. Krishnan, G. S. Kumar, Electrical Measurements on Musa Acuminata Colla, *Uni. J. Ele. Elect. Engi*. Volume 2(8): pp 320-327, **2014**.

[20] A. Rahman and F.H. Stllinger, Molecular dynamic study of liquid water, *J. Chem. Phys*, vol **55**, pp 3336-3359; **1971.**

[21] K, Zhong, C C Yu et al, Vibrational mode frequency correction of liquid water in density functional theory molecular dynamics simulations with van der Waals correction, *Phys.Chem.Chem.Phys*., vol **22**, pp 12785-12793, **2020**.

[22] Md. Abdul Basheer, G Prasad and N V Prasad, Voigt Fitting is of Special Interest for Impedance and Raman Spectroscopic Analysis for Two-Layered Aurivillius Compound, *Int. J. Sci. Res. Phys App Sci*., vol. **8(2)** pp 01-05, **2020**

[23] J.R. Macdonald, *Impedance spectroscopy*, (John Wiley and Sons, New York), **1987**.

[24] A.K. Jonscher, *Dielectric relaxation in solids*, (Chelsa Dielectric Press, London) 1983.

[25] Eric Esch, Walter Neal Simmons, Georgy Sankin, Hadley F. Cocks, Glenn M. Preminger and Pei Zhong, A simple method for fabricating artificial kidney stones of different physical properti*es, Urological Research*. Vol **38**, pp 315-319, **2010.**

[26] Yean-Chin Tsay, 'Application of infrared spectroscopy to analysis of urinary calculi', *The J. Uriology*, vol **86 (6),** pp 838-854, **1961**.

[27] G. Kanchana, P. Sundaramoorthi, and G.P. Jeyanthi Bio-Chemical Analysis and FTIR-Spectral Studies of Artificially Removed Renal Stone Mineral Constituents, *J. Minerals & Mat Cha & Eng*. Vol **8**, pp 161-170, **2009.**

AUTHORS PROFILE

D. Aparna working as Assistant Professor in the Department of Physics, Osmania University, Hyderabad. Her research interests include ferroelectric and ferroelastic materials.

Jabbar Chyad Atiyah has studied M.Sc., (Bio-Physcs), from Nizam college (one of the constituent college of Osmania University). Presently he is working as a teacher in Iraq.

Kaleem Ahmed Jaleeli working as Assistant Professor and Head, Department of Physics, Nizam College, Osmania University, Hyderabad. He was awarded as Fellow of IBS, UK. His specialization is biophysics and he published over 60 research papers in international journals.

Majid Adil has completed MBBS, MS, MCH (Urology) and working as a faculty in Deccan Medical College, Hyderabad. He is an Urologist and consultant to New Life Hospital, Hyderabad, India.

N. V. Prasad working as Assistant Professor, in Department of Physics, Osmania University, Hyderabad. His research interest includes ferroelectric and magnetoelectric materials. He has published more than 55 international journals.