Impedance Spectroscopic Studies of Pure and Zinc Doped Calcium Pyrophosphate Dihydrate Nano-particles

Sonal R. Vasant[1] and M.J. Joshi[2]

[1]L. E. College, Morbi, Gujarat, India
[2]Department of Physics, Atmiya University, Gujarat, India
E-mail:sonalvasant@rediffmail.com

Abstract: Bio-materials are non-viable materials generally possessing osteo-conductivity, non-toxicity, non-inflammatory and non-immunogenicity, which are used in devices for biological system. Calcium phosphate-based bio-materials find important clinical applications such as bone substitution materials and in dentistry. Ionic substitutions have been used as a tool to improve the biological performance of calcium phosphate materials, particularly; zinc improves the activity of osteo-blasts and promotes bone regeneration. As the electric field can accelerate the healing of the fractures and enhances rate of bone growth, the impedance spectroscopic study is an important tool investigate the electrical behaviour of calcium phosphate biomaterials. Pure and Zn doped Calcium Pyrophosphate Dihydrate (CPPD) nano-particles with [Zn]/[Ca] molar ratio as 0 % (Pure CPP), 2 %,5% and,10 % were synthesized by surfactant mediated approach. The nano structured nature of the samples was confirmed by applying Scherrer's formula to Powder XRD patterns and by TEM study. The synthesized samples were characterized by dielectric spectroscopic studies as a function of frequency at different temperatures. The variations in various dielectric parameters like real and imaginary part of dielectric constant, a.c. conductivity, dielectric loss, electric modulus with the frequency of applied field in 3.2 kHz to 32 MHz range and within a temperature range from 30 ^{0}C to 120 ^{0}C were studied. Activation energy was calculated using a.c. conductivity data. The results are discussed.

Keywords: Non-viable, Dentistry, Osteo-blasts, Dielectric Spectroscopy

INTRODUCTION

Bio-materials are non-viable materials, generally possessing properties like osteo-conductivity, non-toxicity, non-inflammatory and non-immunogenicity, are used in devices intended to interact with biological system. Bio-materials can be passive or can be bio-compatible. Bio-compatibility is the ability of material to elicit an appropriate response in the host, for example, bone replacement material to promote the growth of bone tissue. Calcium phosphate-based bio-materials play an important role in clinical applications, especially, as a bone substitution material[1] and as a mild abrasive agent in dentistry[2]. Nano-crystalline materials have received extensive attention due to their unique physical, chemical and mechanical properties; these parameters certainly play important roles in the biological behaviours of calcium phosphate compounds[3]. Calcium Pyrophosphate (CPP) – a shortest linear polyphosphate can also be used as a bone graft material[4].A detailed review article is written on this material by Vasant and Joshi[5]. Various ionic substitutions have been proposed as a tool to improve the biological performance of calcium phosphate-based materials with attention focused on several ions, including Si, Sr, Mg, Zn and Mn[6]. Zn is an essential element in human body; it can stimulate enzyme activity, nucleic acid metabolism and protein synthesis[7]. In case of bone repairing, the presence of Zn ion improves the activity of osteoblasts and promotes bone regeneration[8]. Zn doped Hydroxyapatite and Tri-calcium Phosphate nano-particles are well reported[9, 10]. The present authors have earlier synthesized pure and 2%, 5% and 10 % Zn doped CPP nano-particles by using surfactant mediated approach and characterized them by EDAX, powder XRD, TEM, FT-IR and TGA which is discussed elsewhere in detail[11]. As electric field can accelerate the healing of fracture in bone[12] and enhances the rate of bone growth for bone grafts in spinal fusion [13, 14], in the present investigation the authors intend to carry out impedance spectroscopic studies on pure and zinc doped CPP nano particles to study their response at different frequency of applied field in the temperatures.

EXPERIMENTAL TECHNIQUE

Surfactant mediated approach, discussed in detail elsewhere[15] was used to synthesize pure and Zn doped CPPD nano-particles. AR grade chemicals were used for the synthesis. The 0.5 M aqueous solutions of calcium nitrate tetra- hydrate ($Ca(NO_3)_2.4H_2O$) and $ZnCl_2$ were prepared in such a way that the [Zn]/[Ca] molar ratio varied as 0% (Pure CPPD), 2%,5%,10 %. The 0.25 M aqueous solution of sodium pyrophosphate ($Na_4P_2O_7$) was added in a drop-wise manner into the mixture of Ca $(NO_3)_2.4H_2O$, $ZnCl_2$ and surfactant with constant stirring at 50 ^{0}C. The water to surfactant ratio was maintained as 5:1. A non-ionic surfactant Octoxynol 9 was used. The resulting

precipitates were quickly filtered; washed with the deionized water and air dried. The nano structured nature of pure and Zn doped CPP nano-particles were confirmed by applying Scherrer's formula to Powder XRD patterns and taking TEM images. This has been reported in detail in earlier work[11]. The silver coated pelletized samples which replicate a capacitor were used for the dielectric study. The data were measured by using commercially available impedance analyser (SOLARTRON IMPEDANCE GAIN PHASE ANALYZER SI- 1260) in the frequency range from 3.2 kHz to 32 MHz and within the temperature range from 30 ^{0}C to 120 ^{0}C using small resistive heater attached to the sample holder.

RESULTS AND DISCUSSION

The electrical conductivity and dielectric behaviour of nano-crystalline materials depend on chemical compositions, preparation conditions and grain size[16]. Nano-crystalline materials exhibit enhanced electrical properties compared to their bulk poly-crystalline counterparts. Microwave dielectric properties of pure CPP crystals are reported by Bian[17] and dielectric study of the gel grown monoclinic –CPP tetrahydrate crystals were reported by Parekh and Joshi[18]. Dielectric studies of strontium pyrophosphate[19], nickel pyrophosphate[20] and strontium doped hydroxyapatite[21] are well reported. The studies of dependence of dielectric constant and ac conductivity on frequency of applied field give valuable information about the conduction phenomenon in nano structured materials[22].

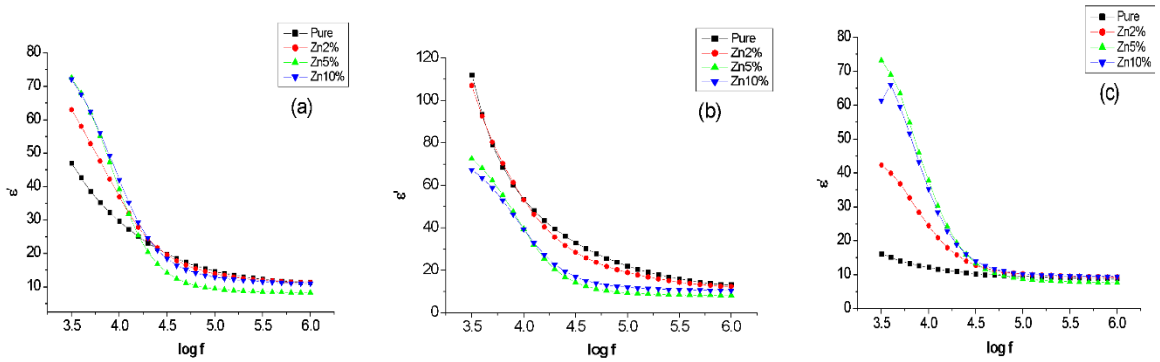

Fig.1-(a) Variations of Dielectric Constant at 30 ^{0}C (b) at 60 ^{0}C & (c) at 120 ^{0}C with the frequency of applied field.

Figure:1-a to c show the variations of dielectric constant with frequency of applied field at 30 ^{0}C, 60 ^{0}C, 120 ^{0}C, respectively. Initially, the dielectric constant decreases rapidly with increasing the frequency and then reaches constant value at higher frequency range above 100 kHz, which is a typical behaviour. The dielectric behaviour of the nano-structured material is primarily due to different types of polarizations present in the material[23]. The nano structured materials have large number of interfaces and also large number of defects present in these interfaces, which is responsible for change in the positive or negative space charge distribution. On applying electric field these space charges move and get trapped by the defects resulting in formation of dipole moment, which termed as space charge polarization. The interface of nano structure material has several oxygen ion vacancies equivalent to positive charges giving rise to dipole moments. On application of an external electric field the dipoles rotate and give resultant dipole moment in the direction of applied field, which is known as rotational polarization. The high value of dielectric constant at low frequency region is mainly due to the presence of space charge and rotational polarizations present in CPP nano-particles. This has been extensively discussed by Indulal and Raveendran[24]. It has been also observed that as doping concentration increases the value of dielectric constant decreases irrespective of temperature variations. This may be due to the small polarizability value of Zinc (38.8 ± 0.3 a.u.) compared to Calcium (169.0 ± 17 a. u.)[25, 26]. For pure CPPD, dielectric constant increases with increase in temperature range upto 60 ^{0}C, this may be due to the fact that as the temperature increases more and more dipole will be oriented resulting in an increased value of dipole moment[27]. However, above 60 ^{0}C as the temperature increases the molecules have more thermal energy and therefore, the amplitude of random motion is greater. This means that the molecules are less closely aligned with each other even in the presence of an electric field. Hence, dielectric constant decreases[28].

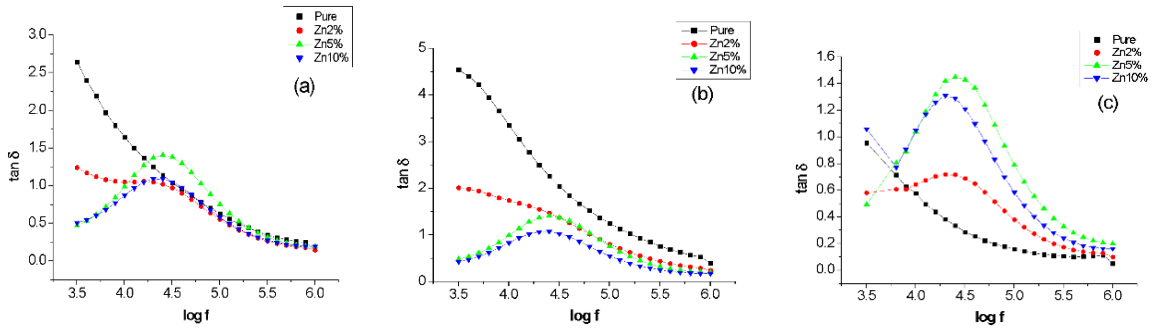

Fig.2-(a) Variations of dielectric loss at 30 ^{0}C, (b) at 60 ^{0}C and (c) 120 ^{0}C with the frequency of applied field

Nearly similar trend is observed for dielectric loss with temperature as that of dielectric constant with temperature. A rise in the loss factor is observed from room temperature to 60 ^{0}C (figure 2-(a & b)), for pure CPPD nano-particles which may be due to increase in the ionization of the sample with temperature increases the conductivity processes and dissipation factor simultaneously. However, above 60 ^{0}C the loss value decreases for pure sample (Figure:2-©) may be due to transition from amorphous to crystalline state, which eventually decreases conductivity and hence dielectric loss[29]. The higher value of dielectric loss at low frequency is due to the free charge motion within the materials, however, at temperature 120 ^{0}C loss value decreases which reflect the chemical and micro-structural quality of the samples[30] and on the addition of Zn content the loss peak shifts towards higher frequency side. Additionally, pure CPPD and 2 % Zn doped CPPD do not exhibit loss peak within the frequency range confirms absence of hopping resonance within the experimental frequency range, however, for higher concentration of Zn when the hopping frequency is approximately equal to that of the externally applied electric field; i.e. it means, resonance phenomena; loss peak is observed[31]. AC conductivity was calculated using formula,

$$\sigma_{a.c.} = 2\pi fCdt/A$$

where, f is frequency, C is the capacitance, d is the diameter, t is thickness and A is the area of the pellet
Figure 3 (a) shows the electrical a.c. conductivity of pure and Zn doped CPP nano-particles with frequency of applied field at 30 ^{0}C, (b) at 60 ^{0}C and (c) 120 ^{0}C with the frequency of applied field. The low-conductivity value at low frequencies is related to the accumulation of ions due to the slow periodic reversal of the electric field[32]. The ac conductivity gradually increases with the frequency; the conductivity in low frequency region is associated with successful hops, beyond the low frequency region many hops are unsuccessful. This change in ratio of successful to unsuccessful hops result in dispersive conductivity. It can be attributed to the fact that the increment in the frequency enhances the electron hopping frequency[33]. Moreover, the ac conductivity decreases with increase in doping concentration. It may be recognized to the fact that dopant introduce defect in pure CPP nano-particles. This facilitates the formation of grain boundary defect barrier leading to the blockage of flow of charge carriers[34]. However, a.c. conductivity for pure and Zn doped CPP nano-particles decreases as the temperature increases which may be due to the loss of water. The reverse nature was observed for the a. c. resistivity.

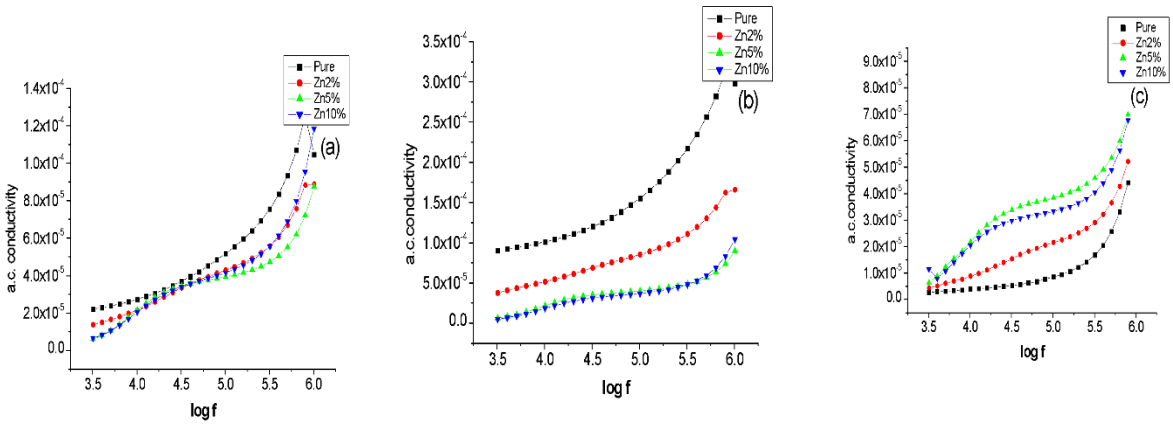

Fig.3-(a) Variations of a.c. conductivity at room temperature, (b) at 60 ^{0}C and (c) 120 ^{0}C with the frequency of applied field

High frequency variations of conductivity are found to obey universal Jonscher's power law behaviour, σ=K ω^n, with $0 \leq n \leq 1$. The exponent n represents the degree of interaction between mobile ions with the lattice around them[35]. The obtained value of n for pure and Zn doped CPP nano-particles are shown in Table (1), which lies between 0 to 1.

TABLE I FREQUENCY EXPONENT COMPONENT "n" OBTAINED FROM JONSCHER'S POWER LAW

Sample	Temperature			
	30 ^{0}C	60 ^{0}C	90 ^{0}C	120 ^{0}C
Pure CPPD	0.20	0.18	0.23	0.34
Zn-2 % CPPD	0.31	0.24	0.32	0.41
Zn-5% CPPD	0.46	0.47	0.45	0.27
Zn-10 % CPPD	0.50	0.55	0.58	0.30

A better way of displaying the frequency and temperature dependence of a.c. conductivity is to present the a.c. conductivity data in the form of Arrhenius plots at different frequencies[36]. From the Arrhenius equation the conductivity can be interpreted as[37],

$$\log(\sigma) = -\,Ea\log(e)/1000k * [1000/T] + \log(\sigma_0)$$

Where, e=2.71828182, σ_0 is the pre-exponential factor and k is the Boltzmann Constant

An attempt was made to calculate activation energy from the slope of log (σT) vs 1000/T[38]. The values of activation energy at different frequencies are given in Table 2.

TABLE II ACTIVATION ENERGY VALUES (eV)FOR PURE AND DOPED CPPD NANO-PARTICLES

Sample	Frequency (Hz)			
	1 x 10^6	1 x 10^5	1 x 10^4	1 x 10^3
Pure CPPD	0.51	0.68	0.71	0.88
Zn-2 % CPPD	0.20	0.29	0.43	0.48
Zn-5% CPPD	0.11	0.12	0.15	0.44
Zn-10 % CPPD	0.06	0.09	0.15	1.93

It is clear that the value of a.c. conduction activation energy decreases with increasing frequency. This can be explained that at low frequencies the overall conductivity is due to the mobility/transportation of charge carriers over long distance rather than from relaxation/orientational mechanism, in which case charge mobility/transportation is restricted to only the nearest neighbouring lattice sites[39].

Complex modulus analysis is an alternative and important approach to explore electrical properties of the material and magnify other effects if present. This helps in determining, analysing and interpreting the dynamical aspects of electrical transport phenomena (i.e. parameters such as carrier/ion hopping rate, conductivity relaxation time, etc.)[39]. The advantage of complex impedance spectroscopy study is that it can identify the role of electrode polarization and grain boundary conduction processes. In the present study, electric modulus M' and M'' were calculated using equation $M' = \epsilon' / (\epsilon'^2 + \epsilon''^2)$ and $M'' = \epsilon'' / (\epsilon'^2 + \epsilon''^2)$[40].

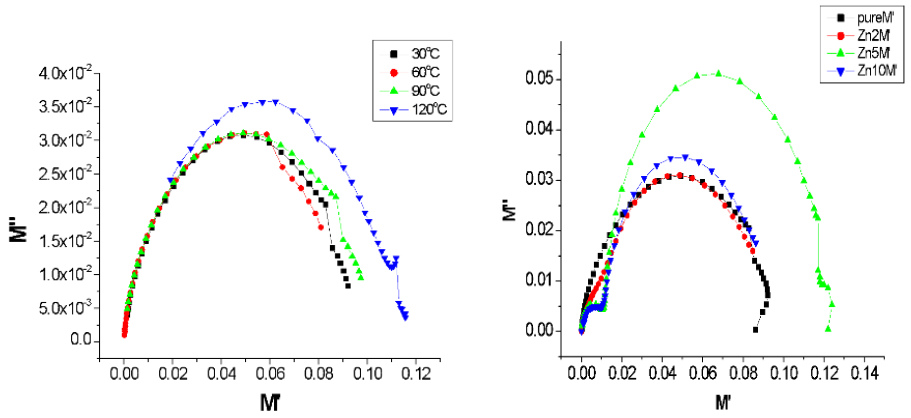

Fig. 4-(a) Complex modulus spectra of pure CPPD nano-particles at various temperatures and (b) Complex modulus spectra of pure and Zn doped nano-particles at 30 ^{0}C.

Figure:4-(a) shows complex modulus spectra of pure CPP nano-particles at various temperatures. It can be seen that as temperature increases, the radius of semi-circle increases this may be due to increase in the dominance of the grain-boundary effect. Figure:4-(b) shows the complex modulus spectra for pure and different Zn doped CPP nano-particles at 30 ^{0}C. In which, 5% and 10% Zn doped CPPD nano-particles show two semicircular arcs in the complex modulus plots with a small semicircle at low frequency corresponding to grains and very large semicircular arc in the high-frequency region which corresponds to grain boundaries, thereby showing the maximum dominance of grain boundaries over the grains[40].The grain boundaries act as hinderance to the transport of charge carriers. Same nature is observed in given temperature range.

CONCLUSION

In the present study a.c. conductivity, dielectric constant and dielectric loss were calculated from the measured capacitance and dissipation data of pelletized samples of pure and Zn doped nano calcium pyrophosphate. Real and imaginary components of electric modulus were calculated from real and imaginary part of dielectric constant. For pure and doped CPP nano-particles dielectric constant and dielectric loss decrease as the frequency is increased. Also, both quantities increase with increment in temperature range upto 60 ^{0}C and above that temperature these values decrease. The a. c. conductivity increased as the frequency of applied field increased and is found to obey Jonscher's universal power law, however, as doping concentration increases conductivity decreases. Activation energy values decrease with increment in frequency. Complex modulus spectra suggested dominance of grain and grain boundary. The temperature and Zn doping has pronounced influence on the dielectric properties of CPPD nano-particles.

ACKNOWLEDGMENTS

The authors are thankful to the Physics Department, Saurashtra University, Rajkot, India. Authors (SRV and MJJ) are thankful to the authorities of Lukhdhirji Engineering College, Morbi, Gujarat and Atmiya University, Rajkot, respectively for their help and motivation.

REFERENCES

1. D. Knaack, M. E. P. Goad, M. Aiolova, C. Rey, A. Tofighi, P. Chakravarthy and D. D. Lee, J. Biomed. Mater. Res., vol. 43, pp. 399–409, 1998.
2. M. Cordon and J. Norfleet, United States Patent, 3989814, 1976.
3. S. R. Radin and P. Ducheyne, J. Biomed. Mater. Res., vol.28, pp.1303-1309, 1994.
4. J. H. Lee, D. H. Lee, and H. S. Ryu, B. S. Chang, K. S. Hong, C. K. Lee, Key Eng Mater., vol. 240-2, pp. 399–402, 2003.
5. S. R Vasant and M. J. Joshi, Rev. Adv. Mater. Sci. vol. 48, pp. 44-57,2017.

6. E. Boanini, M. Gazzano, A. Bigi, Acta Biomater., vol. 6, pp. 1882-94, 2010.
7. M. Yamaguchi, H. Oishi, Y. Suketa, Biochem Pharmacol., vol.37, pp. 4075–80, 1988.
8. W. J. Bettger and B. L. O'Dell, J. Nutr. Biochem., vol. 4, pp. 194-207, 1993.
9. K. P. Tank, P. Sharma, D. K. Kanchan and M. J. Joshi, Cryst. Res.Technol., vol. 46(12), pp. 1309–1316, 2011.
10. M. Li, X. Xiao, R. Liu, C. Chen, L. Huang, J Mater. Sci. Mater. Med., vol.19, pp.797–803, 2008.
11. S. R. Vasant and M. J. Joshi, Eur. Phys. J. Appl. Phys., vol.53, pp.10601-10607, 2011.
12. R. I. Abeed, M. Naseer, E. W. Abel, J. Orthop. Trauma, vol.12 (7), pp. 510-513, 1998.
13. M. Oishi, S. T. Onesti, Neurosurgery, vol. 47, pp. 1041-1055, 2000.
14. C. B. Goodwin, C. T. Brighton, R.D. Guyer, J. R. Johnson, K. I. Light, H. A. Yuan, Spine, vol. 24, pp.1349-1356, 1999.
15. M. Uota, H. Arakawa, N. Kitamura, T. Yoshimura, J. Tanaka, T. Kijima, Langmuir, vol. 21(10), pp. 4724-4728, 2005.
16. A. N. Patil, M. G. Patil, K. K. Patankar, V. L. Mathe, R. P. Mahajan and S. A. Patil, Bull. Mater. Sci., vol. 23 (5), pp. 447- 452, 2000.
17. J. Bian, D. Kim and K. S. Hong, J. Eur. Ceram. Soc., vol. 23(14), pp. 2589-2592, 2003.
18. B. B. Parekh and M. J. Joshi, Cryst. Res. Technol., vol. 42, pp. 127-132, 2007.
19. P. D. Solanki , S. R. Vasant , K. P. Tank , and M. J. Joshi, AIP Conf. Proc., vol.1536, pp.191-192,2013.
20. P. D. Solanki, Mahatta H. Oza, H. O. Jethwa, Jaydeep Joshi, Girish Joshi, R. Jayavel and M. J. Joshi, Nano, vol. 17 (07), 2250049, 2022.
21. K. P. Tank, B. V. Jogiya, D. K. Kanchan and M.J. Joshi, Solid State Phenomena, vol. 209, pp 151-155, 2014.
22. Mo C, Yuan Z, Zhang L and Xie C, Nanostruct Mater, vol. 2, pp. 47-54,1993.
23. M. Chi-Mei, Z. Lide and W. Guozhong, Nanostuctr. Mater., 6, pp. 823-826,1995.
24. C. R. Indulal and R. Raveendran, Indian J. Pure and Appl Phys, vol. 48, pp. 121-126, 2010.
25. T. M. Miller, and B. Bederson, Phys. Rev., vol. A14, pp. 1572-1573, 1976.
26. S. D. Goebel, U. Hohm, and G. Maroulis, Phys. Rev., vol. A54, pp.1973-1978, 1996.
27. K. S. Udupa, P. M. Rao, S. Aithal, A. P. Bhat and D. K. Avasthi, Bull. Mater. Sci. vol. 20, pp. 1069-1077, 1997.
28. M. Shakir, B. K. Singh, R. K. Gaur, B. Kumar, G. Bhagavannarayana, M.A. Wahab, Chalcogenide Letters, vol. 6(12) pp. 655-660, 2009.
29. D. K. Pradhan, R. N. P. Choudhary, B. K. Samantaray Int. J. Electrochem. Sci., vol.3, pp. 597 – 608, 2008.
30. S. R. Vasant and M. J. Joshi, Mod. Phys. Lett. B, vol.25(1) pp. 53-62, 2011.
31. S. F. Mansour, *Egypt. J. Solids, vol. (28), No. (2),* Frequency and Composition Dependence on the Dielectric Properties for Mg-Zn Ferrite *(2005)*
32. K. P. Tank, B. V. Jogiya, D. K. Kanchan and M.J. Joshi, Solid State Phenomena vol. 209, pp. 151-155, 2014.
33. A.K. Roy, K. Prasad and A. Prasad, ISRN ceramics, 369670, 2013.
34. J. P. Gittings, C. R. Bowen, I. G. Turner, F. Baxter and J. Chaudhuri, J. Eur. Ceam. Soc., vol. 27, pp.4187-4190, 2007.
35. A. K. Jonscher, Nature, vol.267, pp.673-679,1977.
36. H. Mahamoud, B. Louati, F. Hlel and K. Guidara, Bull. Mater. Sci., vol.3, pp**.**1069-1075, 2011.
37. L.A. Rodriguez,W. O. Bucheli, H. Correa, J. E. Diosa and R. A. Vargas, La Revista Latinoamericana de Metalurgia y Materials, vol. 3,pp. 1205-1210, 2009.
38. S. A. Acharya and K Singh, Adv. Mat. Lett. vol. 5, pp. 61-66, 2014.
39. S. A. Jawad, H. M. Abdel-Halim, H. M. Shehadeh and A. B. Hallak, Indian J. of Chem., vol. 43A, pp.1181-1185, 2004.
40. A. K. Roy, A. Singh, K. Kumari, K. Prasad and A. Prasad, *IOSR J of App. Phys. (IOSR-JAP)* vol. *3*5, pp.47-58, 2013.