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Dielectric Spectroscopic Studies of Pure and Ionic Substituted Calcium Pyrophosphate Dihydrate Nano-particles



Abstract: - Calcium pyrophosphate – a kind of calcium phosphate are the non-viable bio-materials, generally, possessing osteo-conductivity, non-toxicity, non-inflammatory and non-immunogenicity. These 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 such bio materials, particularly; zinc improves the activity of osteo-blasts and promotes bone regeneration. 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 behavior of these 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 and dielectric loss with the frequency of applied field in 3.2 kHz to 32 MHz range and within a temperature range from 30 0C to 120 0C 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 material¹ and as a mild abrasive agent in dentistry². 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 compounds³. Calcium Pyrophosphate (CPP) –a shortest linear polyphosphate can also be used as a bone graft material⁴.A detailed review article is written on this material by Vasant and Joshi⁵. 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 Mn⁶. Zn is an essential element in human body; it can stimulate enzyme activity, nucleic acid metabolism and protein synthesis⁷. In case of bone repairing, the presence of Zn ion improves the activity of osteoblasts and promotes bone regeneration⁸. 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 detail¹¹. As electric field can accelerate the healing of fracture in bone¹² 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.

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EXPERIMENTAL TECHNIQUE

Surfactant mediated approach, discussed in detail elsewhere¹⁵ 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 ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and ZnCl_2 were prepared in such a way that the $[\text{Zn}]/[\text{Ca}]$ molar ratio varied as 0% (Pure CPPD), 2%, 5%, 10 %. The 0.25 M aqueous solution of sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) was added in a drop-wise manner into the mixture of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, ZnCl_2 and surfactant with constant stirring at 50 °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 work¹¹. 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 °C to 120 °C using small resistive heater attached to the sample holder.

RESULTS AND DISCUSSION

The electrical conductivity and dielectric behavior of nano-crystalline materials depend on chemical compositions, preparation conditions and grain size¹⁶. Nano-crystalline materials exhibit enhanced electrical properties compared to their bulk poly-crystalline counterparts. Microwave dielectric properties of pure CPP crystals are reported by Bian¹⁷ and dielectric study of the gel grown monoclinic –CPP tetrahydrate crystals were reported by Parekh and Joshi¹⁸. Dielectric studies of strontium pyrophosphate¹⁹, nickel pyrophosphate²⁰ and strontium doped hydroxyapatite²¹ 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 materials²².

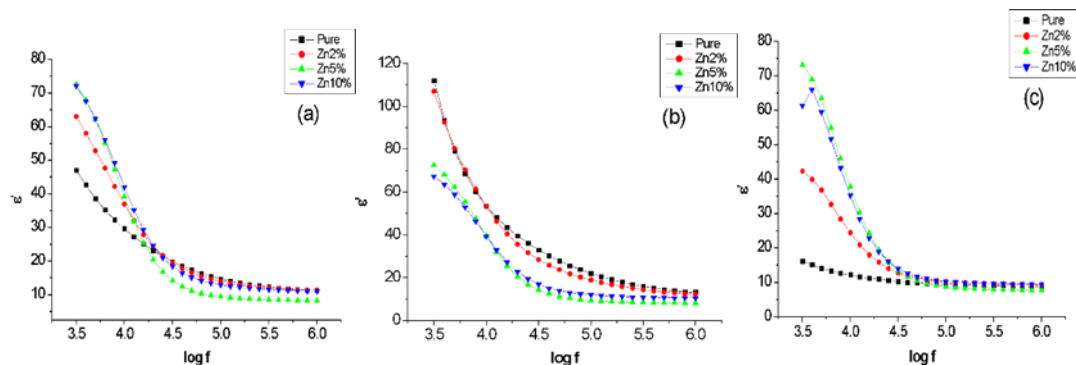


Fig.1-(a) Variations of Dielectric Constant at 30 °C (b) at 60 °C & (c) at 120 °C with the frequency of applied field.

Figure:1-a to c show the variations of dielectric constant with frequency of applied field at 30 °C, 60 °C, 120 °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 material²³. 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 Raveendran²⁴. 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

± a.u.) compared to Calcium (169.0 ± 17 a. u.)^{25, 26}.

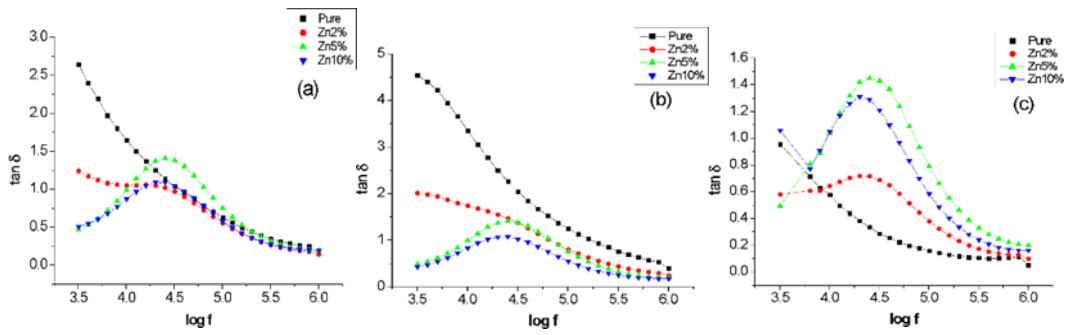


Fig.2-(a) Variations of dielectric loss at 30 °C, (b) at 60 °C and (c) 120 °C with the frequency of applied field

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 °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 °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 loss²⁹. The higher value of dielectric loss at low frequency is due to the free charge motion within the materials, however, at temperature 120 °C loss value decreases which reflect the chemical and micro-structural quality of the samples³⁰ 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 observed³¹. AC conductivity was calculated using formula,

$$\sigma_{a.c.} = 2\pi f C d t / A$$

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 °C, (b) at 60 °C and (c) 120 °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 field³². 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 frequency³³. 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 carriers³⁴. 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.

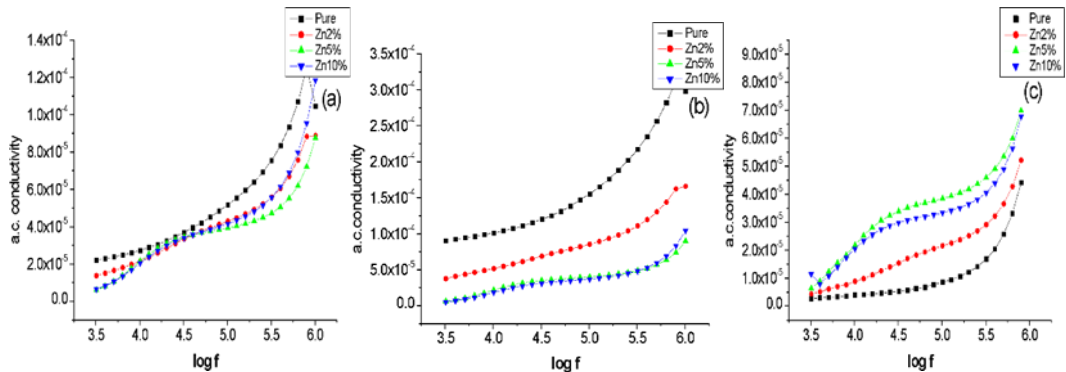


Fig.3-(a) Variations of a.c. conductivity at room temperature, (b) at 60 °C and (c) 120 °C with the frequency of applied field

High frequency variations of conductivity are found to obey universal Jonscher's power law behaviour, $\sigma = K \omega^n$, with $0 \leq n \leq 1$. The exponent n represents the degree of interaction between mobile ions with the lattice around them³⁵. The obtained value of n for pure and Zn doped CPP nano-particles are shown in Table (I), which lies between 0 to 1.

TABLE I FREQUENCY EXPONENT COMPONENT “n” OBTAINED FROM JONSCHER’S POWER LAW

Sample	Temperature			
	30 °C	60 °C	90 °C	120 °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 frequencies³⁶. From the Arrhenius equation the conductivity can be interpreted as³⁷,

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

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 $\log(\sigma T)$ vs $1000/T$ ³⁸. The values of activation energy at different frequencies are given in Table II.

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 sites³⁹.

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

Sample	Frequency (Hz)			
	1×10^6	1×10^5	1×10^4	1×10^3
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

CONCLUSION

In the present study the various dielectrical parameters like 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. 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 °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. The

temperature and Zn doping has pronounced influence on the dielectric properties of CPPD nano-particles.

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