

List of Figures

Fig. 1.1	: Structure of the present dissertation	9
Fig. 2.1	: Compact bone represented in a hierarchical structure from micro to nanometer scale.	20
Fig. 2.2	: Scanning electron microscopic image of the cross-section of a compact bone depicting the Harvesian systems.	21
Fig. 2.3	: Typical hysteresis loop for dry human bone specimen, representing ferroelectricity at 20°C.	26
Fig. 2.4	: Schematic representation of a cell membrane consisting of bilipid layer and proteins.	28
Fig. 2.5	: (a) Parallel combination of voltage gated channels of Na^+ , K^+ , Ca^{2+} , and Cl^- , represented as a series combination of resistance and a battery, Na-K pump represented as a current source and a lipid bilayer represented as a capacitor, (b) electrical equivalent circuit of a cell membrane.	30
Fig. 2.6	: a) Schematic illustrating the monoclinic hydroxyapatite (HA) with space group $P2_1/b$ along $[110]$ direction, b) Hexagonal HA with space group $P6_3/m$ along $[\bar{1}100]$ direction. In both the structures, the orientation of hydroxyl (OH^-) ions is different, c) Two-dimensional enlarged high resolution transmission electron microscopic image of monoclinic HA along $[\bar{1}110]$ direction (upper inset) as well as hexagonal HA along $[100]$ direction (lower inset), and a unit cell of HA (left inset) respectively.	32
Fig. 2.7	: (a) Hexagonal lattice of HA with order-disorder arrangement of OH^- ions, (b) depicts the Polarized HA, (c) - (e) represents the mechanism of formation of surface charges via proton (H^+) migration as well as reorientation of defect dipole polarization under the application of E-field. (f) Orientation of OH^- ions as well as of defect dipoles at different temperatures.	42
Fig. 2.8	: Schematic illustration of the orientation of the hydroxyl (OH^-) ions with respect to Ca^{2+} triangles. (a) Energy scale of the non-polar $P2_1/b$ monoclinic phase, polar $P2_1$ monoclinic phase and polar $P6_3$ hexagonal phase, (b) phase transition from paraelectric to ferroelectric phase. The paraelectric phase is depicted as the $P6_3/m$ hexagonal as well as $P2_1/b$ monoclinic phase.	46
Fig. 2.9	: TSDC spectra of polycrystalline monoclinic HA with different polarization parameters such as polarizing field (E_p), polarizing temperature (T_p) and polarizing time (t_p). (a) $E_p = 0 - 6.2$ MV/m, $T_p = 473$ K, $t_p = 30$ min. (b) $E_p = 1.5$ MV/m, $T_p = 300 - 493$ K, $t_p = 30$ min. (c) $E_p = 1.5$ MV/m, $T_p = 473$ K, $t_p = 5 - 30$ min. The inset in (a) depicts	47

the polarization P_A (area of the sharp peak).

- Fig. 2.10 : Schematic representing the pyroelectric effect in the polycrystalline HA with non-polar and polar grains. Non-polar grains are represented as arrows in antiparallel orientation while parallel arrows represent polar grains. 49
- Fig. 2.11 : Scanning electron microscopic images demonstrating the functionality of human fetal osteoblast cells on negatively (a, b), unpolarized (c) and positively (d) polarized HA surfaces. 52
- Fig. 3.1 : a) Schematic illustrating the electrical equivalent circuit of cell membrane. b) A generalized electrical equivalent circuit for a single living cell with cell membrane as a leaky dielectric, each section of a living cell is represented by a corresponding electrical component in a circuit (model 1). c) Model 2 represents the other ionic pathway (left hand side) under the applied electric stimulation. R_s and C_s represent the resistance and capacitance of extracellular matrix (ECM), respectively. E_m represents the membrane potential, C_m and C_n represent the cell and nuclear membrane capacitances, R_{c1} , R_{c2} and R_{c3} represent the cytoplasmic resistances and R_n is the nucleoplasmic resistance. 91
- Fig. 3.2 : Variation of time constant with cell size at a few selected nucleus to cell size (r_n/r_o) ratios. 97
- Fig. 3.3 : Variation of time constant with capacitance of cell and nuclear membranes for models 1 and 2. 98
- Fig. 3.4 : Variation of time constant with a) resistances of cytoplasm and nucleoplasm and b) cell membrane resistance. 99
- Fig. 3.5 : Variation of electric field, required for electroporation, with various critical membrane potentials: a) 0.7 V, b) 1 V and c) 1.5 V. 103-104
- Fig. 3.6 : Electrical equivalent circuit of single living cell by considering cell and nuclear membranes as leaky dielectrics. (a) and (b) refer to different ionic paths. 109
- Fig. 3.7 : Variation of time constant with a) cell size, b) capacitances of cell and nuclear membranes, c) cytoplasmic and nucleoplasmic resistances and d) resistances of cell and nuclear membranes. 112
- Fig. 3.8 : Variation in current (b) and voltage (c) across the cell and nuclear membranes due to application of pulsed stimulation of strength and duration of 1 V and 1 ms (a), respectively. 114
- Fig. 3.9 : Variation in current (b) and voltage (c) across the cell and nuclear membranes due to application of pulsed stimulation of strength and duration of 1 V and 1 μ s (a), respectively. 115

- Fig. 3.10 : Variation in current (b) and voltage (c) across the cell and nuclear membranes due to application of pulsed stimulation of strength and duration of 1 V and 1 ns (a), respectively. 116
- Fig. 4.1 : Thermal sintering cycle, followed during spark plasma sintering of hydroxyapatite (HA), $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN) and HA-25 vol % NKN composite. 129
- Fig. 4.2 : Schematic illustration of the methodology, utilized for the thermally stimulated depolarized current measurement (TSDC). 132
- Fig. 4.3 : X-ray diffraction spectra for calcined as well as sintered (a) HA and (b) $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (NKN), and (c) HA – 25 vol % NKN composite. 138
- Fig. 4.4 : Scanning Electron Microscopic images of fractures surfaces of SPSeD (a) HA, (b) NKN and (c) HA-25 vol % NKN composite. 139
- Fig. 4.5 : Thermally stimulated depolarization current (TSDC) spectra for HA, polarized at E-field strength of a) 30 kV/cm, b) 50 kV/cm and c) 90 kV/cm, respectively. The depolarization current was measured, while heating the polarized samples at heating rates of 1, 5 and 10°C/min, respectively. 141
- Fig. 4.6 : Deconvoluted TSDC spectra of HA, depolarized at the heating rate of 10°C/min after polarization at a) 30 kV/cm and b) 90 kV/cm. The respective Arrhenius plots (a)-(i), (a)-(ii), (b)-(i) and (b)-(ii) depicting the activation energies, obtained from deconvoluted spectra. 143
- Fig. 4.7 : Schematic representing the (a) arrangement of hydroxide (OH^-) ion in the hexagonal unit cell, (b) the proton rotation model indicating the mechanism of polarization and depolarization from left to right and (c) the migration of protons by rotation around the O^{2-} ions to the adjacent proton vacancy site. 146
- Fig. 4.8 : Schematic illustration of (a) proton migration along c-axis in the applied field direction from left to right and (b) the process of dehydration and consequently, the diffusion of oxide (O^{2-}) ions from upper to lower sites after dehydration and thereafter, lower to upper sites along c-axis. 147
- Fig. 4.9 : Schematic representation of the polarization process occurring in the polycrystalline HA with different grain sizes and similar carrier density. Pattern 1 depicts the accumulated charge after polarization without the hindrance of the grain boundaries and Pattern 2 reveals the influence of grain boundaries on the accumulated charge, after polarization. 149
- Fig. 4.10 : Schematic representation of mechanism of formation of defect pair dipoles: (a) HA crystal having no OH^- defect, (b) creation of OH^- and H^+ defects on dehydroxylation, (c) Subsequent transfer of protons for 151

realignment of defect pair dipoles and (d) aligned defect pair dipoles along the E-field.

- Fig. 4.11 : Schematic illustrating the mechanism of space charge formation in HA, 152
 (a) proton defects present randomly in the grains, (b) E-field application transfers the protons in the specified direction and accordingly accumulating on the grain boundaries.
- Fig. 4.12 : (a) Variation of dielectric constant (ϵ_r) and loss (D) as well as (b) ac 155
 conductivity with temperature at 100 kHz of frequency for the unpolarized and polarized (90 kV/cm) HA. (c) Variation of ac conductivity with inverse of temperature for the unpolarized and polarized HA.
- Fig. 4.13 : X-ray photoelectron spectroscopy (XPS) spectra of polarized and 158-
 unpolarized HA. (a)-(i) , (a)-(ii) Adventitious carbon (C-C) along with 159
 the presence of O-C=O group is depicted by binding energies of ~284 and ~287 eV. The presence of (b)-(i), (b)-(ii) calcium 2p orbital state, (c)-(i),(c)-(ii) Oxygen 1s orbital state and (d)-(i),(d)-(ii) Phosphorus 2p orbital state is depicted in both, the polarized and unpolarized HA.
- Fig. 4.14 : TSDC spectra of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$, (a) polarized at 30, 50 and 90 kV/cm, 161
 respectively and depolarized at a heating rate of 1 °C/min, (b) polarized at 90 kV/cm and depolarized at heating rates of 1, 5 and 10 °C/min, respectively, (c) variation of dielectric constant (ϵ_r) and loss (D) as well as (d) ac conductivity response with temperature at 100 kHz of frequency for unpolarized and polarized $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ (90 kV/cm).
- Fig. 4.15 : (a) TSDC spectra of HA – 25 vol % NKN composite, polarized at 90 167
 kV/cm, (b) dielectric constant (ϵ_r) and loss (D) as well as (c) ac conductivity behaviour with temperature at 100 kHz of frequency for unpolarized and polarized HA - 25 vol% NKN composite.
- Fig. 4.16 : Deconvoluted TSDC spectra of HA - 25 vol % NKN composite, 169
 depolarized at the heating rate of 1 °C/min. The respective Arrhenius plots (b) and (c) depicting activation energies of deconvoluted spectra.
- Fig. 5.1 : Spatial distribution of different layers in developed FGM, (a) 186
 HA:BT:HA and (b) HA:CT:HA.
- Fig. 5.2 : X-Ray diffraction spectra for (a) HA, BT and FGM HA-BT-HA as well 188
 as (b) HA, CT and FGM HA-CT-HA samples.
- Fig. 5.3 : SEM micrographs illustrating the morphological behaviour of fractured 189-
 surfaces of (a) HA, (b) BT and (c) buffer, interfacial regions between (d) 190
 HA and buffer as well as (e) BT and buffer.
- Fig. 5.4 : SEM micrographs illustrating the morphological behaviour of fractured 191-
 surfaces of (a) HA, (b) CT and (c) buffer, interfacial regions between (d) 192
 HA and buffer as well as (e) CT and buffer.

- Fig. 5.5 : Variation of dielectric constant (ϵ) and loss (D) for (a) HA, (b) HA-BT- 193
HA and (c) HA-CT-HA with temperature at few selected frequencies.
- Fig. 5.6 : Variation of dielectric constant (ϵ) and loss (D) for (a) HA, (b) HA-BT- 195
HA and (c) HA-CT-HA with frequency at few selected temperatures.
- Fig. 5.7 : Variation of AC conductivity for (a) HA, (b) HA-BT-HA and (c) HA-CT- 197
HA with temperature at few selected frequencies.
- Fig. 5.8 : Variation of AC conductivity for (a) HA, (b) HA-BT-HA and (c) HA-CT- 200
HA with frequency at few selected temperatures.
- Fig. 5.9 : Complex plane impedance plots for HA, HA-BT-HA and HA-CT-HA at 204
few selected temperatures (a-f). Variation of resistances of grain (R_G)
and grain boundary (R_{GB}) with inverse of temperature (g).