Dielectric and Pyroelectric Properties of HAp-BaTiO$_3$ Composites

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In order to mimic the electrical properties of natural bone, the present work investigated the dielectric, AC conductivity, pyroelectric and piezoelectric properties of HA-40 wt\% BaTiO\textsubscript{3} (HA-26 vol\% BaTiO\textsubscript{3}) and HA-60 wt\% BaTiO\textsubscript{3} (HA-44 vol\% BaTiO\textsubscript{3}) composites. Multistage spark plasma sintering was used to achieve the desired combination of properties. The electrical parameters were measured as a function of temperature and frequency. The values of dielectric constant and loss for both the developed composites, measured at room temperature and at 1 KHz frequency was 21, 38 and 0.01 and 0.02, respectively. The AC conductivity for both the composites is found to be of the order of $10^{-10}$ and $10^{-9}$ (\textOmega cm)$^{-1}$, measured under similar conditions. Activation energy calculated from $\sigma_{ac}$ vs. temperature plot for HA-40 wt\% BaTiO\textsubscript{3} is 0.50 eV. The room temperature pyroelectric coefficients for both the compositions are 2.35 and 21 $\mu$C m$^{-2}$K$^{-1}$, respectively. The piezoelectric coefficient values ($d_{33}$) for both the compositions are 0.9 and 1 pC/N, respectively. The observed values of electrical parameters closely resemble with that of the natural human bone.

1. Introduction

Hydroxyapatite (HA) is the most widely investigated calcium phosphate biomaterial for orthopaedic applications, as it interacts with host bone by exchanging Ca$^{2+}$ and PO$_4^{3-}$ ions. This helps in stimulating the bone growth and enhances the integration of the implant material with the host bone [1, 2]. Therefore, HA is recognized as highly biocompatible and bioactive material. However, the poor electrical and mechanical properties limit its application as an implant material. On the other hand, natural bone possesses significant piezoelectricity [3], streaming potential [4] and pyroelectricity [5]. The electric potential generated due to piezoelectric effect has an important role in new bone formation [6]. It is, therefore, possible that the addition of a biocompatible piezoelectric component to HA may improve the host response to that implant material.

In this perspective, BaTiO\textsubscript{3} (BT), a piezoelectric material, seems to be potential biomaterial as it can enhance the bone formation in complex physiological environment [7, 8]. BT containing composite (PVDF-TrFE/BT) has also been found as in vivo biocompatible material after testing in rabbit tibiae [9]. Apart from improving the electrical properties with
the addition of ferroelectric phase, Chen et al. [10] suggested that a piezoelectric secondary phase can improve the toughness of composite due to the energy dissipation and domain wall’s motion. It is, therefore, expected that the addition of BT in HA may improve the mechanical and electrical response of developed biocomposite.

In order to exploit the known bioactivity of HA and electrical activity of BT, two composites HA-40 wt% BT (H4B6) (HA-26 vol% BaTiO3) and HA-60 wt% BT (H2B4) (HA-44 vol% BaTiO3) have been optimally processed using spark plasma sintering technique. The purpose of this study is to examine the dielectric, piezoelectric and pyroelectric properties of the developed composites and compared these properties with the natural bone. The temperature and frequency variation of dielectric constant, loss and AC frequency has also been discussed.

2. Experimental

2.1 Materials Synthesis

HA is synthesized by widely reported suspension-precipitation route [11, 12]. HA powders were then calcined at 1073 K for 2 hrs and the XRD peaks confirmed the pure hydroxyapatite phase.

For the preparation of BaTiO3, stoichiometric amounts of BaCO3 and TiO2 were weighed and mixed in a ball mill using agate balls as grinding media and acetone as a milling medium for 6 hrs in agate jar. The mixed powders were dried overnight in oven. The dried powders were calcined at 1273 K for 6 hrs in a platinum crucible. For composites, HA-40 wt% BT (HA-26 vol% BaTiO3) and HA-60 wt% BT (HA-44 vol% BaTiO3) were ball milled for 16 hrs in wet medium (acetone) using agate balls and jar as milling media. The purpose of the milling was the homogeneous mixing of particles and reduction of initial particle size.

The multistage spark plasma sintering route was adopted to consolidate the powder compact. The spark plasma sintering process can densify a ceramic body in a very short duration and at a lower temperature [13]. The sintering of HA at a lower temperature (∼1273 K) was required to inhibit a deficiency of OH− ions in HA structures and this will have an implication on electrical and biological properties. The sintering cycle is shown in Fig. 1. In this approach, initially the powder compact was held for 5 min. at a temperature of 0.4 Tm (Tm is the average melting point of both the phases) to promote the initial surface activation, then heated to a temperature 0.5 Tm and hold it there for 5 min, followed by the heating to 0.57 Tm without holding. The samples were then furnace cooled. The heating rate was kept at 373 K/min. Such processing condition has been reported to result in uniform and better mechanical properties of the ceramics [14, 15].

2.2 Materials Characterization

The capacitance and loss were measured using an automated measurement system having an LCR meter (HP-4284 A, Hewlett-Packard). The measurements were done in the temperature range 173 K-423 K at frequencies between 100 Hz and 1 MHz. The samples were heated at heating rate of 5 K/min. The pyroelectric measurements were made using the Byer–Roundy method [16]. The samples were poled while slowly cooling from 403 K temperature to 173 K and applying a field of 10 kV/cm. After poling, the samples were electrically shorted for 5 minutes before collecting the pyroelectric data. A picoammeter (HP- 4140B, Hewlett
Figure 1. Sintering cycle used during multistage spark plasma sintering of composites.

Packard Inc.) was used to monitor the pyroelectric current produced by the samples, while heating at a constant rate (~3 K/min). The piezoelectric measurements were conducted using Berlin Court d33 meter.

3. Results and Discussion

3.1 Dielectric Behavior

Plots of dielectric constant ($\varepsilon_r$) and dielectric loss (D) with temperature in the temperature range of 173–423 K at a few selected frequencies for both the compositions are shown in Fig. 2. Plots of $\varepsilon_r$ and D with frequency for these compositions at a few temperatures are shown in Fig. 3. It is observed that the permittivity value increases with increase in the temperature at a given frequency. However, an increase of $\varepsilon_r$ and D with temperature is much more significant at lower frequencies than at higher frequencies. This may be due to the development of interfacial polarization in the presence of two phases with different electrical conductivities. The permittivity value decreases with increase in frequency and the high frequency plateau is weakly dependent on temperature.

The relative permittivity exhibits a frequency dispersion in which the magnitude decreases with increasing frequency. This may be due to the presence of conductivity in the material, most probably the ionic conduction at high temperatures. A common phenomenon that occurs during the sintering of this composite is the partial decomposition of HA due to the dehydroxylation (removal of OH$^{-}$ ions). At high temperatures OH$^{-}$ ions are responsible for conduction.

In Figs. 2(a) and (b) D vs. T plots for both the compositions show the similar behavior. At higher frequencies (>100 KHz), a low temperature plateau (upto 300 K) appears which is followed by a temperature dependent region. The plateaus extend to higher temperature with increasing frequencies. In the D vs. log f plots, no peak is obtained in any of the curves. Thus, relaxation time $\tau$ cannot be calculated from these plots. However, a diffuse maxima for high temperatures (373 and 423 K) is seen, which is the signature of some kind of relaxation occurring in the composite at 100 KHz.
Figure 2. Variation of dielectric constant ($\varepsilon_r$) and loss (D) with temperature at a few selected frequencies for composition (a) HAp-40 wt% BaTiO$_3$ and (b) HAp-60 wt% BaTiO$_3$.

The permittivities of the developed composites were calculated using parallel and series Wiener bounds [17] using eq. (1) and (2)

$$\varepsilon_{\text{composite}} = V_{HA}\varepsilon_{HA} + V_{BT}\varepsilon_{BT}$$  \hspace{1cm} (1)

$$\frac{1}{\varepsilon_{\text{composite}}} = \frac{V_{HA}}{\varepsilon_{HA}} + \frac{V_{BT}}{\varepsilon_{BT}}$$  \hspace{1cm} (2)

Where, $\varepsilon$ is the permittivity of the material and $V$ is the volume fraction (HA and BT refer to hydroxyapatite and BaTiO$_3$). The calculated permittivity values for both the developed composites using eq. (1) are 295 and 490 (at 1 KHz), respectively. However, the calculated
Figure 3. Variation of $\varepsilon_r$ and $D$ with log frequency at a few steady temperatures for composition (a) HAp-40 wt%BaTiO$_3$ and (b) HAp-60 wt%BaTiO$_3$.

The permittivities of these composites by considering the series Wiener bound are 16 and 21 (at 1 KHz), respectively.

Logarithmic mixture rule [18] for the dielectric constant of a polyphase material is given as eq. (3)

$$\log \varepsilon_r = \Sigma_i V_i \log \varepsilon_i$$  (3)
This gives a value between the series and parallel Wiener bounds. The calculated permittivity values for both the developed composites using eq. (3) are 38.8 and 87.6 (at 1 KHz) respectively.

The electrical and mechanical properties of composite are influenced by the connectivity of the constituent phases [19]. It can be seen that there is a considerable decrease in permittivity of the composite in comparison to high dielectric constant phase BT (∼1100 at 1 KHz). This may be due to the isolation of ferroelectric phase by HA particles. Here, we consider 0–3 connectivity between the ferroelectric and HA phase of the developed composite. Figure 4 represents the schematic diagram showing the 0–3 connectivity between both the phases. Landauer [20] expression for 0–3 connectivity in a binary system is valid for large volume fraction of second phase and hence, should be appropriate for H₆B₄ and H₄B₆ composites.

The Landauer equation is

$$V_1 \frac{(\varepsilon_1 - \varepsilon_c)}{(\varepsilon_1 + 2\varepsilon_c)} + V_2 \frac{(\varepsilon_2 - \varepsilon_c)}{(\varepsilon_2 + 2\varepsilon_c)} = 0 \quad (4)$$

Where, $V_1$ and $V_2$ are the volume fractions of two different phases, $\varepsilon_1$ is the dielectric constant of piezoelectric phase and $\varepsilon_2$ is that of continuous phase, where $\varepsilon_2 >> \varepsilon_1$, $\varepsilon_c$ is the dielectric constant of the composite. For our case, the value of above expression for H₆B₄ at 100 Hz is 0.13 and 0.12 for higher frequencies. For H₄B₆, it is 0.24 at 100 Hz and 0.23 for higher frequencies.

Jayasundere and Smith [21] derived an expression for dielectric constant of the composite having 0–3 connectivity by taking into account the interaction between piezoelectric spheres.

$$\varepsilon = \frac{\varepsilon_1 V_1 + \varepsilon_2 V_2 \left[ \frac{3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \right] \left[ 1 + \frac{3V_2(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + 2\varepsilon_1} \right]}{V_1 + V_2 \left[ \frac{3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \right] \left[ 1 + \frac{3V_2(\varepsilon_2 - \varepsilon_1)}{\varepsilon_2 + 2\varepsilon_1} \right]} \quad (5)$$
As the interaction between the piezoelectric phases increases with increase in the concentration of second phase. The above expression is found to be valid for higher volume fraction of the second phase.

The Maxwell-Garnet [22] expression for the effective permittivity ($\varepsilon_{\text{eff}}$) of a polyphase material is given as,

$$
\varepsilon_{\text{eff}} = \frac{\varepsilon_m V_m \left[ \frac{2}{3} + \frac{\varepsilon_i}{3\varepsilon_m} \right] + \varepsilon_i V_i}{V_m \left[ \frac{2}{3} + \frac{\varepsilon_i}{3\varepsilon_m} \right] + V_i}
$$  \hspace{1cm} (6)

Where, $V_m$ and $\varepsilon_m$ are the volume fraction and dielectric constant of the matrix phase and $V_i$ and $\varepsilon_i$ are the volume fraction and dielectric constant of the inclusion phase. For the present case, measured values of dielectric constant are not in full agreement with the values predicted by this theory.

Figure 5 represents the comparison of dielectric constant obtained from eq. (5) and (6) with the present study at a few selected frequencies at room temperature. It is observed that for H$_6$B$_4$, the values of dielectric constants are very close (<4% deviation at 1 KHz and higher frequencies) to that obtained from eq. (5) for all the measuring frequency range.

The dielectric constant of the human cortical bone has been found to be a very sensitive function of water content [23]. The dielectric constant of dry human cortical bone is around 10. However, the room temperature value of dielectric constant and loss for both the developed composites, H$_6$B$_4$ and H$_4$B$_6$ are 21, 38 and 0.01 and 0.02 respectively.

### 3.2 AC Conductivity Behavior

AC conductivity was measured as a function of frequency and temperature. The plots of $\log \sigma_{\text{ac}}$ vs. $\log f$ at a few selected temperatures and $\log \sigma_{\text{ac}}$ vs. 1000/T at a few selected frequencies are shown in Figs. 6 & 7. At low temperature, the conductivity is almost independent of temperature and depends strongly on frequency. However, in the high temperature region, the $\log \sigma_{\text{ac}}$ varies linearly with temperature, obeying the Arrhenius equation, $\sigma = \sigma_0 \exp \left(-\frac{E_a}{kT}\right)$, where $E_a$ is the activation energy for conduction. For H$_6$B$_4$, a diffuse maxima is seen in $\log \sigma_{\text{ac}}$ vs.1000/T plot, before the high temperature linear region for the frequencies up to 1 KHz. This may be due to the dielectric relaxation. The plot of $\log \sigma_{\text{ac}}$ vs.1000/T at the frequency of diffuse maxima for H$_6$B$_4$ is shown in Fig. 8. The plot is found to be linear. The value of activation energy from this plot is 0.50 eV.

It is observed that the conductivity increases with increasing frequencies [Fig. 6(a)]. The temperature up to which conductivity remains constant decreases with decrease in frequency [Fig. 6(b)]. Thus, it is inferred that at high frequency, conductivity is almost constant at low temperature and increases only at high temperature. However, at low frequencies, conductivity increases with increasing temperature uniformly.

The experimentally recorded behavior of $\log \sigma_{\text{ac}}$ vs. $\log f$ (at different steady temperatures) for H$_6$B$_4$ and H$_4$B$_6$ is essentially similar. From the slope of the dispersion region, it is inferred that the temperature dependence of AC conductivity increases, but its frequency dependence decreases with increasing temperature. At high temperature, conductivity is almost frequency independent, but linearly dependent on temperature.

AC conductivity with frequency varies linearly with frequency at all measuring temperatures. However, there is a little signature of plateau in the curve at higher frequencies,
which is beyond our measuring range [Fig. 6(a)]. It is therefore, evident that the linear (dispersion) region represents some relaxation process. In case of H₄B₆ [Fig. 6(b)], AC conductivity increases linearly with frequency in the measuring frequency range.

Although the composites were sintered at low temperature, but because of momentary generation of spark of plasma, local temperature is high [24, 25]. Due to this, a small loss of oxygen from BT or OH⁻ ion from HA is possible. Such defects potentially rise to the localized energy levels between valence and conduction band.

The dependence of AC conductivity on frequency can be explained by the following mechanisms [26]:

\[ \varepsilon_r \]
Figure 6. Variation of log $\sigma_{ac}$ with (a) log frequency and (b) inverse of temperature for the composition HAp-40 wt%BaTiO$_3$.

(a) Transport by carriers excited to localized states near band edge and hopping at energy close to it. Here, the dependence of AC conductivity with temperature is given by

$$\sigma_{ac} \propto \exp\left[-(E_F - E_A)/KT\right]$$ (7)

(b) Hopping of charge carriers in the localized states near the Fermi level, the corresponding expression is

$$\sigma_{ac} \propto T$$ (8)

Shamos and Lavine [27] have reported that the electrical properties of the dry bone lies between the good insulator and poor semiconductor. The dielectric constant of dry bone sample at 100 KHz varies from 8 to 9.2 [28].
Figure 7. Variation of log $\sigma_{ac}$ with (a) log frequency and (b) inverse of temperature for the composition HAp-60 wt%BaTiO$_3$.

In the present study, the AC conductivity for both the composites is found to be of the order of $10^{-10}$ and $10^{-9}$ (Ωcm)$^{-1}$ respectively. This is the same order as reported by Reinish et al.[29] for dry bone. AC conductivity of dry human femur is $10^{-10}$ Ω$^{-1}$ cm$^{-1}$.

3.3 **Pyroelectric and Piezoelectric Behavior**

The pyroelectric coefficient was calculated from the pyroelectric current by:

$$ p = \frac{i}{A \left[ \frac{dT}{dt} \right]} $$

(9)
where \( p \) is the pyroelectric coefficient, \( i \) is the pyroelectric current, \( A \) is the electrode area, and \( \frac{d\mathcal{T}}{dt} \) is the heating rate. The polarization was calculated by the pyroelectric coefficient:

\[
P_s = \int p\,dT
\]  

Figure 9 shows the pyroelectric coefficient and spontaneous polarization for both the compositions as a function of temperature. In case of H$_6$B$_4$ (Fig. 9(a)), the pyroelectric coefficient reaches its maximum value, 8.6 \( \mu \)C/m$^2$ K at temperature of 393 K. This temperature corresponds to the maximum polarization change and phase transition. The other phase transitions are clearly noticeable at 331.6 K and 278.6 K, where the peak values of the pyroelectric coefficients are 4.3 \( \mu \)C/m$^2$ K and 2 \( \mu \)C/m$^2$ K, respectively. The maximum polarization, as determined from pyroelectric measurement, was 0.84 mC/m$^2$ at 100 K. The polarization then slowly decays to 0.76 at 174 K. With further increase in temperature, the polarization decreases rapidly and finally, attains a small value.

In case of H$_4$B$_6$ (Fig. 9(b)), the phase transitions at 380 K and 270 K are clearly evident, where the peak value of the pyroelectric coefficients are 85 \( \mu \)C/m$^2$ K and 29 \( \mu \)C/m$^2$ K, respectively. The maximum polarization, as determined from pyroelectric measurement, was 13.82 mC/m$^2$ at 100 K. The polarization is then slowly decays to 13.5 mC/m$^2$ at 235.64 K. With further increase in temperature, the polarization decreases rapidly.

The room temperature pyroelectric coefficient for both the compositions is 2.35 and 21 \( \mu \)C/m$^2$ K, respectively. Lang [5] reported the pyroelectric coefficient for dry bovine femur to be 0.0036 ± 0.0021 \( \mu \)C/m$^2$ 0°C. The measured room temperature piezoelectric coefficient values (d$_{33}$) for both H$_6$B$_4$ and H$_4$B$_6$ composites are 0.9 and 1 pC/N respectively, which compare well with that observed in bone (0.7 pC/N) [30].
4. Conclusion

The permittivity value increases more rapidly with temperature at lower frequencies (<1 KHz) than at higher frequency. This may be the result of interfacial polarization, which arises due to the presence of two phases with different electrical conductivities. The relative permittivity exhibits a frequency dispersion in which the magnitude decreases with increasing frequency. The frequency dispersion may be attributed to the presence of conductivity in the material, most likely the ionic conduction at high temperatures. The room temperature value of dielectric constant and loss for both the developed composites was [21, 38] and (0.01, 0.02), respectively, measured at 1 KHz of frequency. The significant decrease in the permittivity of the developed composite in comparison to high dielectric constant phase (BaTiO$_3$) may be due to the isolation of ferroelectric phase by hydroxyapatite. In the present study, the AC conductivity for HA-40 wt% BaTiO$_3$ and HA-60 wt% BaTiO$_3$, measured at 1 KHz, is found to be of the order of $10^{-10}$ and...
10^(-9) (Ωcm)^{-1}, respectively. From pyroelectric coefficient measurement, it is confirmed that the phase transitions in the developed composite HA-40 wt% BaTiO_3 occurred at temperatures 393, 331.6 and 278.6 K. These temperatures correspond to the maximum polarization change. The maximum polarization, as determined from pyroelectric measurement, was 0.84 mC/m^2 at 100 K. In case of HA-60 wt% BaTiO_3, the phase transitions occurred at 380 and 270 K are evident. The maximum polarization, as determined from pyroelectric measurement, was 13.82 mC/m^2 at 100 K. The room temperature pyroelectric coefficient for both the compositions is 2.35 and 21 µC/m^2 K, respectively. The room temperature measured piezoelectric coefficient values (d_{33}) for both the compositions are 0.9 and 1 pC/N. From the above mentioned properties, it can be clearly inferred that the developed composite can be a promising material for orthopedic applications, as far as the electrical compatibility of the composite with the bone is concerned.

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