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# Characterisation of ferroelectric-calcium phosphate composites and ceramics

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## Abstract

This paper studies the effect of composite composition on the electrical properties of $BaTiO_3$-hydroxyapatite (HA) composites and examines the high temperature electrical properties of pure HA. At least 80% volume of $BaTiO_3$ was needed for the composites to exhibit any stress-induced piezoelectric potential. At elevated temperatures, pure HA exhibits an increase in real part of conductivity and permittivity. The increased ionic conductivity at elevated temperatures can be used to manufacture polarised HA bioceramics with permanent surface charges as polarised HA exhibited a depolarisation current at elevated temperatures.

*Keywords:* Piezoelectric properties; Ferroelectric properties; Dielectric properties; Composites

## 1. Introduction

Due to the disadvantages associated with bone grafting and bone replacement procedures using autograft and allograft, research into the development of synthetic bone replacement materials has continuously accelerated. A variety of bone replacement materials have been developed, including hydroxyapatite (HA) which is a member of the calcium phosphate family and is the main mineral component found in bone. It interacts with the host bone by exchanging calcium ($Ca^{2+}$) and phosphate ($PO_4^{3-}$) ions to form apatite precipitations on the ceramic substrate. This stimulates bone growth and enhances the integration of the implant material with the host bone.[1,2]

Recent research has found enhanced osteobonding and bone growth on the surface of polarised HA due to the generation of a permanent surface charge on the material *in vitro*.[3–6] It has been demonstrated by Nakamura et al.[7] that apatite crystal growth on HA was accelerated on the negatively charged surface. The surface charge is not due to dipole rotation, as in ferroelectric materials, but is thought to develop from proton migration in the columnar $OH^-$ structure of HA under an applied electric field.[7] In addition to HA polarisation, it is known that bone exhibits intrinsic piezoelectric behaviour[8] and develops a charge under the application of a mechanical stress. It has been hypothesised that stress-induced potentials in bone influence the activity of osseous formation.[9] As a result, piezoelectric materials have attracted interest in medical applications. Park[10] and Hwang et al.[11] examined *in vitro* CaP crystal growth formation on piezoelectric $BaTiO_3$. Calcium phosphate crystals rapidly grew on the negatively charged surface, indicating that polarised $BaTiO_3$ can improve bioactivity. Feng et al.[12] prepared HA-$BaTiO_3$ composites with a piezoelectric $d_{33}$ coefficient of 6pC/N, which promoted osteogenesis in the jawbones of dogs. There was, however, no indication of the precise composition of the composites.

This paper reports the electrical and piezoelectric properties of HA-$BaTiO_3$ composites to elucidate the volume fraction of $BaTiO_3$ necessary to achieve piezoelectric behaviour. Since HA can be polarised[3–6] in the absence of a ferroelectric phase by the application of 1–2 kV/cm at 300 °C,[7] the electrical properties of pure HA at elevated temperatures are also discussed.

## 2. Experimental methods

### 2.1. Hydroxyapatite-barium titanate composite study

HA-$BaTiO_3$ composites were manufactured from HA grade 130 powder supplied by Stryker Orthopaedics and 99.9% pure grade $BaTiO_3$ powder (Ferro). Composites were manufactured via pressureless sintering. After ball milling with a polyvinyl

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alcohol binder, the powder was sieved and compacts were cold pressed at 80MPa. Composites were sintered in air at 1300 °C for 2.5 h with a heating rate of 60 °C/hr. After sintering, the samples were ground flat and silver electrodes were applied. Materials were poled by corona poling at 130 °C using a 28 kV potential and a point source height of 55 mm. The $d_{33}$ coefficient (charge/unit force) was measured using a Take Control PM25 Piezometer. Permittivity and ac conductivity were measured at room temperature from 0.1 Hz–1 MHz using a Solartron 1260 Impedance Analyser and a 1296 Dielectric Interface at $1V_{\mathrm{rms}}$.

### 2.2. Pure HA study

Pure HA specimens were manufactured in the same manner as the composites and the permittivity and ac conductivity of the samples were measured from 0.1 Hz–1 MHz at room temperature to 500 °C. HA polarisation was achieved by the application of an electric field at elevated temperature. The electric field was held at 6 kV/cm for 1h at 500 °C and was maintained until the sample cooled to room temperature. thermally stimulated depolarisation current (TSDC) measurements were used to determine the degree of polarisation of the materials by heating the sample from room temperature to 600 °C at a rate of 2 °C/min and measuring the depolarisation current using a Keithley 6514 picoammeter, a thermocouple and data logger.

## 3. Results and discussion

Fig. 1 shows the variation in the piezoelectric $d_{33}$ charge coefficient as a function of $BaTiO_3$ content. Composites containing less than 80% $BaTiO_3$ exhibited no measurable $d_{33}$ coefficient ($d_{33} = 0$), indicating the lack of piezoelectric properties. Above 80% volume of $BaTiO_3$ the $d_{33}$ coefficient increases until a maximum of 115pC/N at 100% $BaTiO_3$ (Fig. 1). For the HA-$BaTiO_3$ composites the addition of a non-piezoelectric HA ceramic could lead to an increased level of matrix 'clamping', which could account for the rapid decrease in $d_{33}$. This is often observed in ferroelectric-polymer composites[13] and the higher stiffness of the HA could increase the degree of clamping. Barium or calcium substitution from individual phases could also lead to low $d_{33}$.

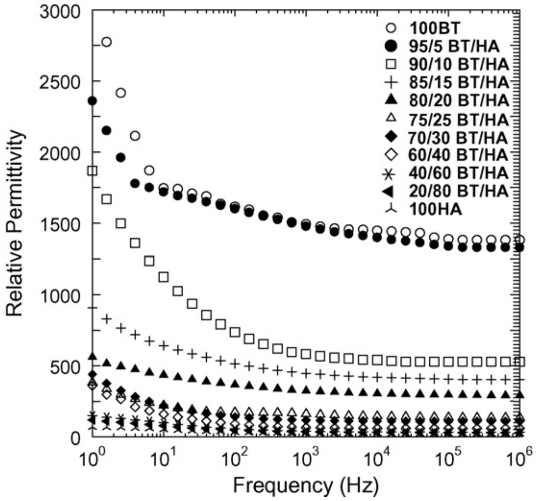

Fig. 2. Relative permittivity of all compositions as a function of frequency.

Fig. 1 also shows the dependence of relative permittivity on composite composition, showing an increase in permittivity as the volume fraction of $BaTiO_3$ increases. Fig. 2 shows the frequency dependent permittivity, indicating that all the samples show a degree of frequency dispersion. The permittivity magnitude and degree of dispersion decreases with decreasing $BaTiO_3$ content, although even pure HA exhibits a dielectric dispersion. Such dispersions are likely to be due to the presence of some dc conductivity in the material,[14,15] although other mechanisms such as the dipole moment of hydroxyl ions in HA have been proposed to explain such effects.[16]

Fig. 3 shows the variation in real part of ac conductivity as a function of frequency for all the composite compositions. At low frequencies (<10 Hz) there is little or no frequency dependence for many of the composites. For higher frequencies (>10 Hz) the conductivity rises almost linearly with frequency (*f*), following the 'universal' power law behaviour[17] such that $\sigma(\omega)\ \alpha\ \omega^n$,

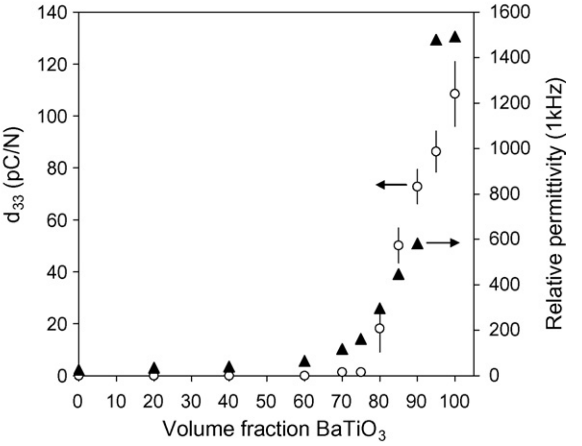

Fig. 1. Piezoelectric charge coefficient ($d_{33}$) at 97 Hz and relative permittivity at 1kHz for HA-$BaTiO_3$ composites.

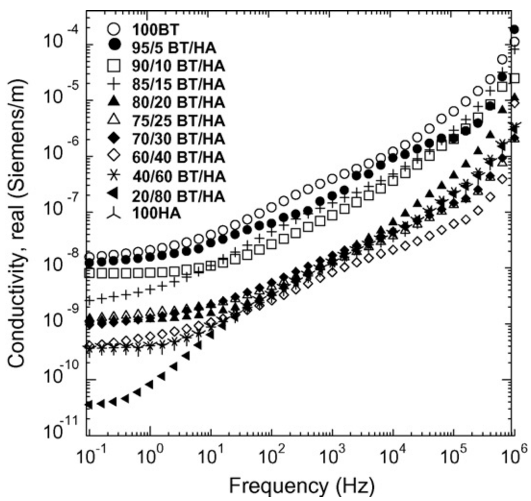

Fig. 3. Real part of ac conductivity for HA-$BaTiO_3$ composites.

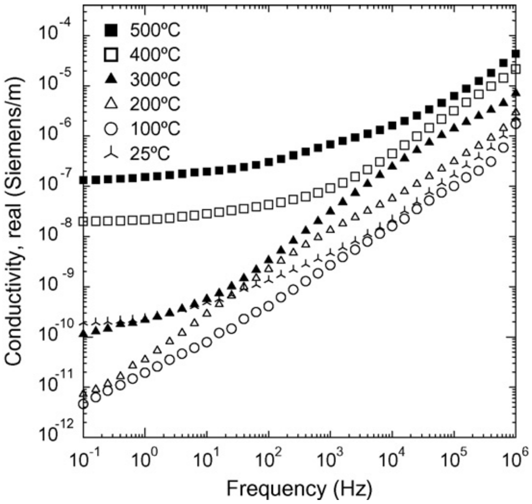

Fig. 4. Real part of ac conductivity for pure HA at elevated temperatures.

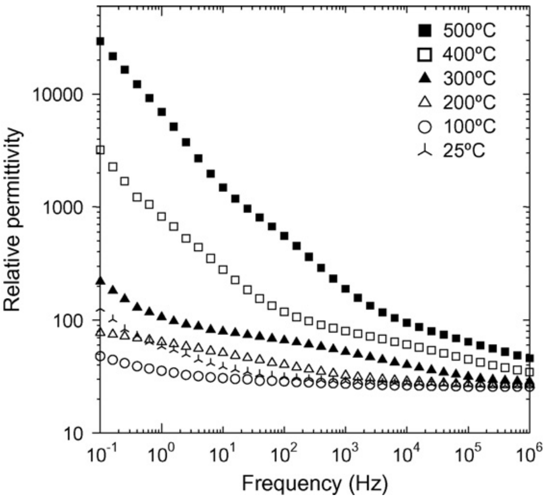

Fig. 5. Relative permittivity as a function of frequency at elevated temperatures for pure HA.

where $\omega$ is angular frequency ($2\pi f$) and $n$ is $0.80 < n < 0.97$. Fig. 3 reveals that, for all the composites studied, the ac conductivity at a particular frequency increases with increasing $BaTiO_3$ content. It has been shown[15] that the ac conductivity (admittance) of the insulating phases, $\omega\varepsilon\varepsilon_0$, can contribute to the conductivity in the power law region, where $\varepsilon$ is the relative permittivity of the phase (HA or $BaTiO_3$) and $\varepsilon_0$ is the permittivity of free space. Since the permittivity of $BaTiO_3$ is much greater than HA (Fig. 1), the higher $\omega\varepsilon\varepsilon_0$ of $BaTiO_3$ leads to an increase in ac conductivity with increasing $BaTiO_3$ content.

Based on these observations, the HA-$BaTiO_3$ composites prepared by Feng et al.[12] with $d_{33}$ of 6pC/N must have contained a significant volume fraction of $BaTiO_3$ (>80%). Therefore the polarisation of pure HA was also examined and will now be discussed.

Fig. 4 shows the frequency dependence of the real part of ac conductivity of pure HA at a range of temperatures. As with the composites, the overall response is characterised by a frequency independent conductivity at low frequencies (<10 Hz), followed by frequency dependent conductivity at higher frequencies (>1 kHz). Examination of the low frequency conductivity (<10 Hz) reveals that from room temperature to 200 °C the conductivity magnitude decreases, possibly due to the loss of water, but then increases in the temperature range of 200–500 °C due to increased ionic conductivity.

Fig. 5 indicates the frequency dependent relative permittivity at a variety of temperatures for pure HA. The permittivity decreases rapidly with frequency and increases with increased temperature, particularly above 300 °C. Such a response is typical of a ceramic or insulating host containing a dc conductivity that increases with temperature.[14,15] Based on the observations in Figs. 4 and 5, temperatures of 300 °C or higher should be used for polarisation of pure HA as there is an increased level of ionic conductivity.

Fig. 6 shows the TSDC curve for both unpoled HA and poled HA. For the poled HA, the depolarisation current increases at ~400 °C current until it reaches a maximum at 540 °C. Under the application of a high electric field at elevated temperatures, the conductivity in pure HA has been attributed to proton migration in the columnar $OH^-$ structure of HA.[18] This result suggests that the polarisation took place due to ionic processes, possibly proton migration in the HA structure. In comparison the unpoled HA sample exhibited no variation in its depolarisation current (see Fig. 6).

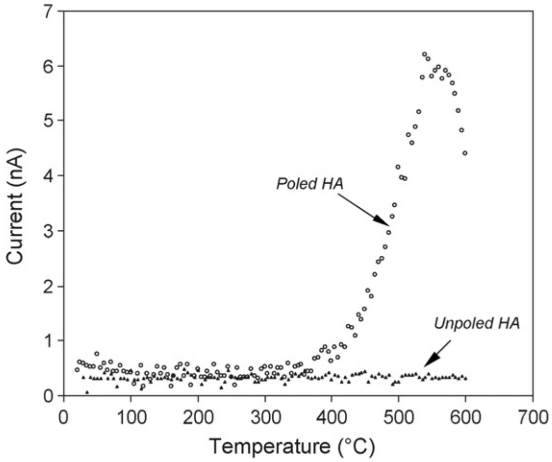

Fig. 6. TSDC curves for unpoled HA and HA poled at 500 °C under an electric field of 6 kV/cm. Sample size: diameter = 13 mm, thickness = 1 mm.

## 4. Conclusions

This paper has investigated two methods of polarising HA materials. The first method involves an examination of the properties of HA-$BaTiO_3$. For the HA-$BaTiO_3$ composites, the $d_{33}$ coefficient decreases rapidly and at least 80% volume $BaTiO_3$ is required for the composites to exhibit a stress-induced piezoelectric potential. The second method involves inducing a polarisation in non-ferroelectric HA. The frequency dependent conductivity and permittivity of pure HA as a function of temperature has been examined. At temperatures above 200 °C there is an increase in conductivity and permittivity. The frequency dependent ac conductivity and permittivity of HA at elevated temperature is typical of a material consisting of conductive and insulating components. HA materials were successfully polarised, as indicated from the measurement of the thermally stimulated depolarisation current.

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