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The Structure and Properties of Electroceramics for Bone Graft Substitution

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Abstract. Hydroxyapatite (HA) and barium titanate (BT) powders were mixed and sintered to form hydroxyapatite – barium titanate (HABT) ceramics. These materials were then poled and their piezoelectric properties were measured. The microstructure of unpoled samples was examined using scanning electron microscopy (SEM).The piezoelectric constants (d_{33} and d_{31}) of the ceramics were found to be dependent on the proportion of BT in the ceramic In materials containing less than 70% BT, no piezoelectric effect was found. Above this value, the piezoelectric constant increased with the addition of BT up to a value of 108pCN^{-1} for pure BT. Values of d_{33} for ceramics containing more than 80% BT are above values previously shown to have a positive influence on bone growth *in vivo*. SEM analysis indicated that the grain size within the materials decreased as the proportion of BT in the material was reduced. Examination of the microstructure of the ceramics indicated the presence of electrical domains in the 100% BT and 95% BT ceramics. Domains were not visible below 95% BT. The reduction in grain size may influence the reduction in piezoelectric activity within the materials but cannot be considered to be the only cause.

Introduction

Stress generated potentials exist in bone in the form of piezoelectricity [1] and streaming potentials [2]. It has been shown that bone growth is influenced by these electromechanical signals [2, 3]. This has led to the suggestion that piezoelectric materials may offer advantages over existing bone graft substitutes although there has been limited research in this area. Calcium phosphate based bone graft substitutes in the form of hydroxyapatite (HA) have wide application in orthopaedic and dental applications as both fillers and coatings and as tissue engineering scaffolds [4]. Feng *et al* [5] examined the biocompatibility of hydroxyapatite - barium titanate (HABT) composites in canine subjects in order to exploit the known biocompatibility of HA and the piezoelectric nature of BT. They found that the composites appeared to promote osteogenesis in canine jawbones. However, there is a need for a better understanding of these materials if they are to be developed for clinical applications. The purpose of this study is to examine the piezoelectric properties and microstructural characteristics of a range of HABT ceramics with varying compositions.

Materials and Methods

The calcium phosphate powder used in this study was manufactured by Thermphos BV (Oldbury, UK). The BT powder was type Terro P, manufactured by Ferro (Haverhill, UK). The powders were mixed in a range of ratios to produce ceramics containing 0, 20, 40, 60, 70, 75, 80, 85, 90, 95, and

100% BT by volume. A volume gauge was used to measure out $0.353 cm^3$ powder for each individual tablet. Tablets were cold pressed in a 15mm die at 60MPa for 10 seconds. They were then sintered at 1300°C for 2.5 hours with a heating and cooling rate of 60°C/hr. Post sintering, tablets measured 13mm in diameter and 3mm in thickness.

For the measurement of piezoelectric properties, tablets were poled using corona poling. The discs were heated to 130°C and exposed to a potential of 25 kV at a point source height of 55mm as they cooled to room temperature. The longitudinal and transverse piezoelectric constants (d_{33} and d_{31}) of the tablets were measured 24 hours after poling using a Take Control Piezometer PM25. Unpoled discs were sectioned vertically and the exposed faces were polished, followed by chemical etching using 10% hydrofluoric acid. A Jeol JSM6310 scanning electron microscopy (SEM) operating with an accelerating voltage of 20kV was used to examine the microstructure of the materials.

Results and Discussion

Measurement of the piezoelectric properties revealed that the magnitudes of the constants (d_{33} and d_{31}) were directly related to the % BT in the ceramic, as shown in Fig.1. Increasing the HA content leads to a rapid decrease in the magnitude of both constants. No piezoelectric effect was found in materials containing less than 70% BT.

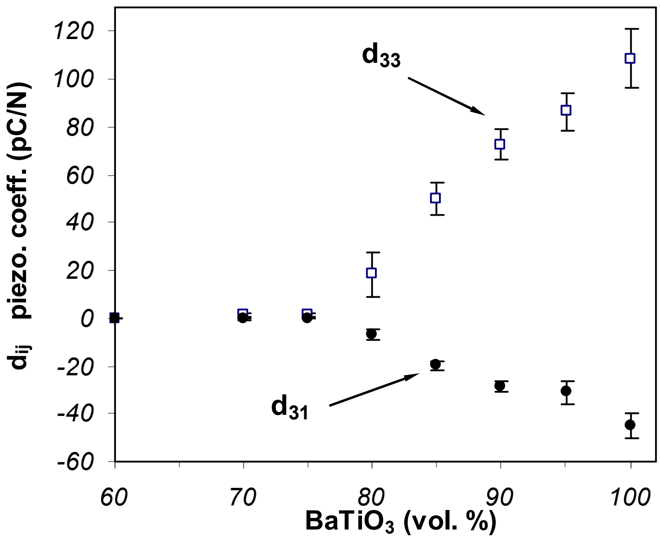
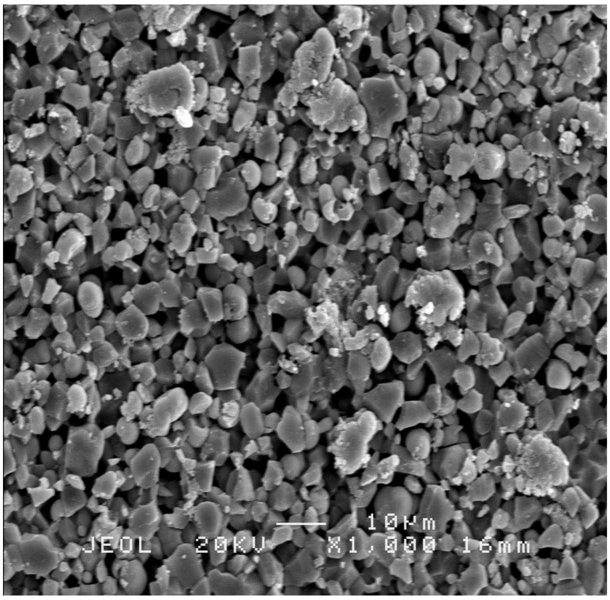


Fig.1 Variation of piezoelectric constants with % BT. Error bars show standard deviation (n=6)

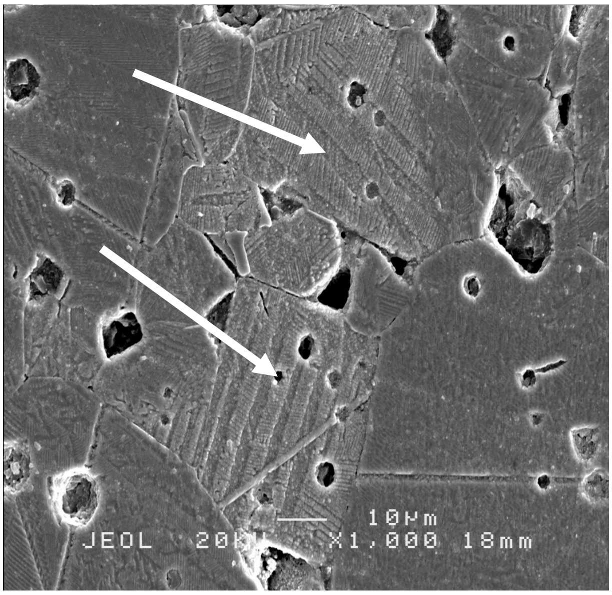
Although the HABT ceramics produced in this study containing 70 and 75%BT have piezoelectric constants below $1 pCN^{-1}$, those containing 80% BT have a d_{33} of $18 pCN^{-1}$. An earlier study by Feng *et al* [5] found bone growth *in vivo* to be influenced by piezoelectric ceramics with a d_{33} of $6 pCN^{-1}$. Similarly, Calegari and Belangero [6] found improved bone growth in piezoelectric polymer tubes implanted in rat femurs when compared to non-polarised tubes. It may therefore be anticipated that HABT ceramics containing 80% or more BT will be capable of inducing a positive bone growth response.

SEM analysis was carried out on a range of samples. Selected images are shown in Fig.2. The SEM micrograph of the pure HA (Fig.2a) shows a fine grained polycrystalline HA structure. In comparison, the microstructure of pure BT (Fig.2b) contains large grains (30-50μm) in which striated ferroelectric domains are clearly visible. Ferroelectric domains are also visible, though less clearly, in the 95% BT ceramic (Fig.2c). At 90% BT ferroelectric domains are no longer apparent (Fig.2d). The presence of ferroelectricity in this material is, however, proven by the results found for the piezoelectric constant, which shows a relatively large d_{33} ($72 pCN^{-1}$) at 90% HA.

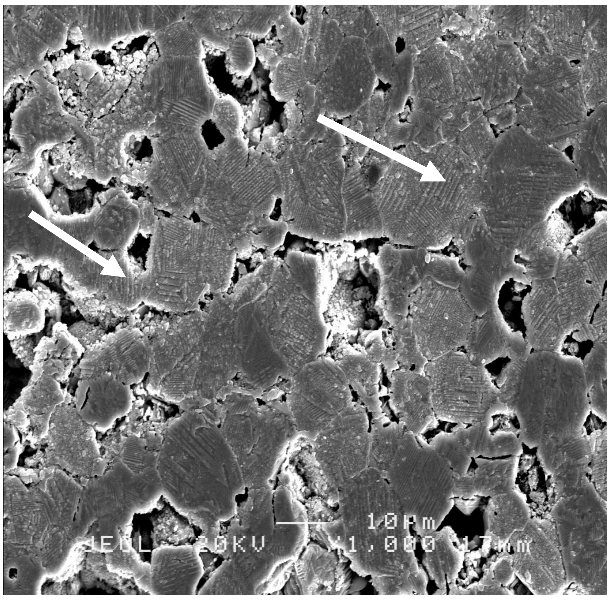
Grains shown in Fig.2b (pure BT) are 30-50µm in size, while in Fig.2c (95% BT) grains measure around 10µm. At 90% BT, grain sizes are reduced to 1-2µm. In other compositions, grain size decreases as the proportion of BT in the ceramic is reduced to zero.



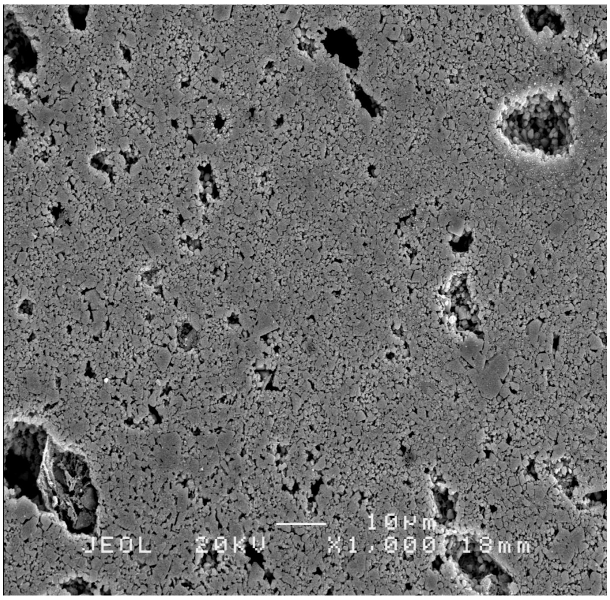
a) 100% HA (0% BT)



b) 100% BT



c) 95% BT



90% BT

Fig.1. SEM micrographs of HABT ceramics. Original magnification x1000. Arrows show ferroelectric domains as indicated by visible striations. Scale bars 10µm.

It appears, therefore, that the reduction in grain size associated with the increase in HA content contributes to the reduction in the piezoelectric constants. This suggestion is supported by the results of an earlier study [7] which found a rapid drop off in d_{33} in lead zirconate-titanate ceramics for grain sizes below 1µm. Cau and Randall [8] found that, in fine grained materials, grain size affects domain wall motion and therefore influences piezoelectric properties. However, though Arlt [9] showed that the domain size in BT is related to the grain size, the link between domain size, grain size and piezoelectric properties in BT ceramics remains unclear for large grain sizes. For example, Takahasha et al [10] found high piezoelectric constants (d_{33}=350pCN^{-1}) in BT ceramics with grains measuring 2.1µm, with no indication that a reduction in grain size leads to a lower d_{33} for grains between 1 and 100µm across. The reduction in piezoelectric properties of the materials examined in the current study cannot, therefore, be attributed to diminishing grain size alone. Further analysis of the composition of the sintered materials is therefore necessary to gain a fuller understanding, including analysis of possible reactions between HA and BT.

Conclusions

HABT ceramics with a range of piezoelectric properties have been produced. The piezoelectric constant (d_{33}) of these materials varies from 0pCN^{-1} at 70% BT to 108pCN^{-1} at 100% BT. The d_{33} of the ceramics containing over 80% BT is in a range that may be expected to influence bone growth *in vivo*. SEM micrographs show that grain size decreased as the proportion of BT in the ceramic is reduced. Electrical domains were clearly visible in ceramics containing 100% and 95% BT. The reduction in grain size in these materials may contribute to, but cannot explain completely, the reduction in the piezoelectric constants of the HABT as the HA content increases.

Further investigation of the composition of these materials after sintering and of the influence of the microstructure and piezoelectric properties of the ceramics on cell responses *in vitro* is planned.

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