Electro-thermally Polarized hydroxyapatite (HAp) Ceramics: Influence of MgO, SrO, and ZnO Dopants

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Statement of Purpose: The objective of this work is to investigate the influence of doping of trace elements (Mg^{2+}, Zn^{2+}, and Sr^{2+}) on polarization behavior of sintered HAp pertinent to biomedical applications. In our previous research we have shown that tailoring the combined effect of surface charge density, surface energy, and surface wettability enable early stage mineralization as well as enhanced cell adhesion and growth on negatively charged HAp compact surfaces [1, 2]. However, one of the major drawbacks of the synthetic HAp is its inferior osteogenic capacity and poor mechanical strength compared to living bone tissue, and this has been attributed to the subtle but significant chemical difference found in the structure. Natural bone contains different trace elements such as such as CO_3^{2-}, Na^+, Mg^{2+}, Zn^{2+} and Sr^{2+} which play an important role in biological and mechanical performances of bone [3]. Therefore, it is important to incorporate these trace elements into synthetic HAp to improve their mechanical and biological performance. In this research, we aim to incorporate these trace elements into HAp structure as dopants which give additional advantage of matching bone chemistry along with the benefit of electrical polarization treatment. We have hypothesized that poling behavior of HAp can be tailored by doping trace elements that have significant influence on structural stability of HAp, and combined influence of dopants and polarization can permit rapid tissue in-growth process.

Methods: Commercially procured phase pure HAp was doped using 0.25wt % ZnO, 1.0wt% SrO and 1.0wt% MgO as dopants in different single, binary and ternary compositions. The amount of dopants was optimized based on our previous calcium phosphate ceramics research [3]. All samples were sintered at 1200°C in an electrically heated muffle furnace for 2h. Phase analysis of sintered samples was performed using X-ray diffraction, and density was measured using Archimedes principle. All sintered samples were electrically polarized under identical poling condition using an external d.c. field (E_v) of 2 $kVcm^{-1}$ for 1h at 400°C (T_p). Thermally stimulated depolarization current (TSDC) technique was used to confirm the success of the polarization treatment. The stored charge (Qp) value for each sample was calculated by integrating individual TSDC curve. *In vitro* bone cell-materials interaction was studied by culturing the polarized samples with osteoblast cells (hFOB).

Results: Our research results reveal that dopants has significant influence on relative density, HAp phase stability as well as polarizability and charge storage ability of sintered HAp compacts. Undoped HAp exhibits a relatively low density (93.1 ± 1.96 %) after sintering compared to single doped or binary doped HAp samples. XRD analysis shows that during sintering undoped HAp was partially decomposed into α-TCP due to dehydroxylation (removal of OH^-) which is a common phenomenon often encountered in sintering of commercial HAp powder. However, the presence of Mg and Sr significantly improved the stability of HAp crystal structure. The influence of MgO and SrO dopants was more pronounced for binary doped (1wt% Mgo-1wt% SrO) HAp where the decomposition of HAp was almost inhibited by combined addition of these two dopants. A maximum relative density of 98.2 ± 1.16 % has been achieved by adding 1 wt% MgO and binary doped HAp (1wt% Mgo-1wt% SrO) samples also exhibit considerable improvement in density (97.6 ± 0.84%). However, both ZnO doped single and ternary HAp samples exhibited low density due to dominant presence of α-TCP. Figure 1 shows the characteristic TSDC thermograms measured for

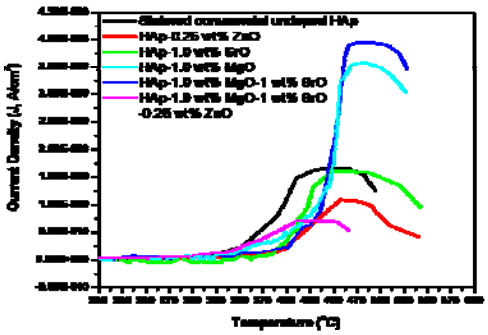

Figure 1. TSDC thermograms obtained for different polarized doped HAp and undoped sintered HAp samples.

different doped and undoped polarized HAp samples. The value of stored surface charge density for the polarized undoped commercial HAp sample has been estimated as 2.23 $\mu C/cm^2$. Interestingly the stored charge density of doped HAp can be seen to gradually increase from 2.37 $\mu C/cm^2$ to 3.86 $\mu C/cm^2$ with the addition of SrO and MgO into Hap, respectively. The maximum current density and stored charge density of 3.95 nA/cm^2 and 4.19 $\mu C/cm^2$ respectively has been achieved for combined addition of MgO and SrO dopants in HAp. *In vitro* cell culture experiments reveal that both MgO and binary doped samples favor rapid cell attachment, proliferation and differentiation over undoped or negatively charged surfaces, while positive charge surfaces show evidence of limited cellular response.

Conclusions: It has been observed that small addition of MgO and combined addition of MgO-SrO are most beneficial in enhancing the polarizability and charge storage ability by inhibiting the HAp phase decomposition. Our research findings establish that combined influence of dopants and polarization can potentially assist in designing of a bone graft material that can be used for better tissue in-growth and rapid initial stability of the HAp based orthopedic implants.

References: [1] Bodhak S, Bose S, Bandyopadhyay A. Acta Biomater 2009;5[6]:2178-2188, [2] Bodhak S, Bose S, Bandyopadhyay A. Acta Biomater 2009 (In press), [3] Bandyopadhyay A, Bernard S, Xue W, Bose S. J Am Ceram Soc 2006;89 [9]:2675-2688.