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Comparative evaluation of electrical conductivity of hydroxyapatite ceramics densified through ramp and hold, spark plasma and post sinter Hot Isostatic Pressing routes

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ABSTRACT

Hydroxyapatite ceramics synthesized through sonochemical route were processed and densified through ramp & hold (R&H) and Spark Plasma Sintering (SPS) routes. The effect of processing route on the relative density and electrical conductivity were studied. Further, the samples were Hot Isostatically Pressed (HIP) under argon pressure at elevated temperature to further densify the sample. All these samples processed under different conditions were characterized by X-ray diffraction, Scanning Electron Microscopy and AC Conductivity. The samples have exhibited hydroxyapatite phase; however, microstructures exhibited distinctly different grain morphologies and grain sizes. AC impedance spectroscopic measurement was carried out on hydroxyapatite samples processed through different routes and the corresponding spectra were analyzed by the analogy to equivalent circuit involving resistors and capacitors. SPS sintered sample after HIPing has exhibited the highest conductivity. This can be attributed to the higher density in combination with finer grain sizes. Activation energy based on Arrhenius equation is calculated and the prominent conduction mechanism is proposed.

1. Introduction

Currently, hydroxyapatite (HAp) is commonly the material of choice in various biomedical applications, e.g. as a replacement for bone [1–2], tissue engineering systems [3–4], drug delivery agent [5] and dental materials [6]. The general importance of HAp and its derivatives have also led to numerous nonmedical industrial and technological applications, e.g. as a catalyst for chemical reactions [7–8], host materials for lasers [9] and ion conductors [10]. The properties of HAp are determined by its chemical composition, structure, particle morphology and crystallite size which are strongly dependant on preparation methods. Recently, HAp ceramics with sintered grains engineered the nano sizes with narrow distribution through controlled sintering parameters had stimulated significant interest due to their superiority for various biomedical applications [11]. Studies on nano-sized HAp bio-ceramics have exhibited enhanced re-absorbability [12–13] and superior bioactivity [14–15] in comparison to their micron-sized counter parts. Major challenges to achieve the nano-grained HAp ceramics lies in the processing of nanopowders, due to their inherently high surface activity leading to agglomeration, while forming. In addition, though nano-scale HAp shows improved densification [16–17] due to better sinterability [17–19], problems associated with micro-cracking and as well as exaggerated grain growth are the issues. Achieving theoretical densities in combination with fine grains is a strong function of conventional and non-conventional densification strategies employed as well as the sintering parameters and schedules. Conventionally ceramics are subjected to densification by ramp and hold (R&H) sintering, which can be modified using rate controlled sintering [20], two-stage sintering [21] and also under simultaneous application of temperature and pressure [22]. Non-conventional sintering methodologies, include Spark Plasma Sintering (SPS) [23–25], Flash sintering [26–27], Microwave based sintering [28], etc. SPS simultaneously applies pulsed electric current and pressure directly on the sample leading to densification at relatively lower temperatures and short retention times. As both the die and sample are directly heated by the joule effect extremely high heating rates are possible.

Hydroxyapatite ceramics, due to their inherent hexagonal crystallography possess hydroxyl ions and atoms in the c-axis oriented channels which are responsible for the electrical conductivity [29]. In addition to the conduction of OH^- ions jumping, O^{2-} and H^+ ions are also contributes to the conductivity of HAp samples. In the case of dense bodies, the microstructure in terms of grain and grain boundary relaxation processes is also expected to have a prominent effect on the properties [30]. Though the biocompatibility and mechanical properties are extensively studied for HAp ceramics, studies on electrical conductivity are limited. Recently, high temperature permittivity of HAp ceramics with the electric field has been used as a tool to study and found a correlation with the enhancement in bone growth [31]. In

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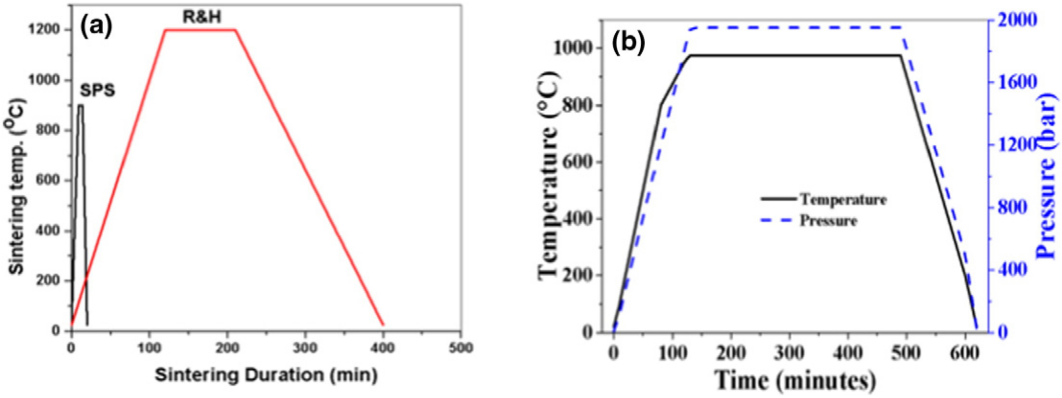

Fig. 1. (a) Sintering Schedule employed for hydroxyapatite pellets for R&H and Spark Plasma Sintering methodologies (b) HIP heating Schedule for R&H and Spark Plasma Sintered samples.

another study, higher electrical conductivity is reported in multi-stage spark plasma sintered HA-$CaTiO_3$ composites by sintering the samples at 1200 °C to achieve the densities greater than 98% [32]. Moreover, the importance of grain size refinement and processing route for final electrical properties was demonstrated in HAp-based bio-ceramic composites [33–34].

The present study attempts a comparative evaluation of densification and microstructure development through the conventional sintering methodologies such as R&H, as well as non-conventional SPS methodology. R&H and SPS processed samples are post-sinter HIPed to achieve densities close to theoretical values. Samples were also subjected to high temperature impedance measurements and the electrical conductivity values of the samples were found to exhibit a strong correlation with grain and grain boundary structure.

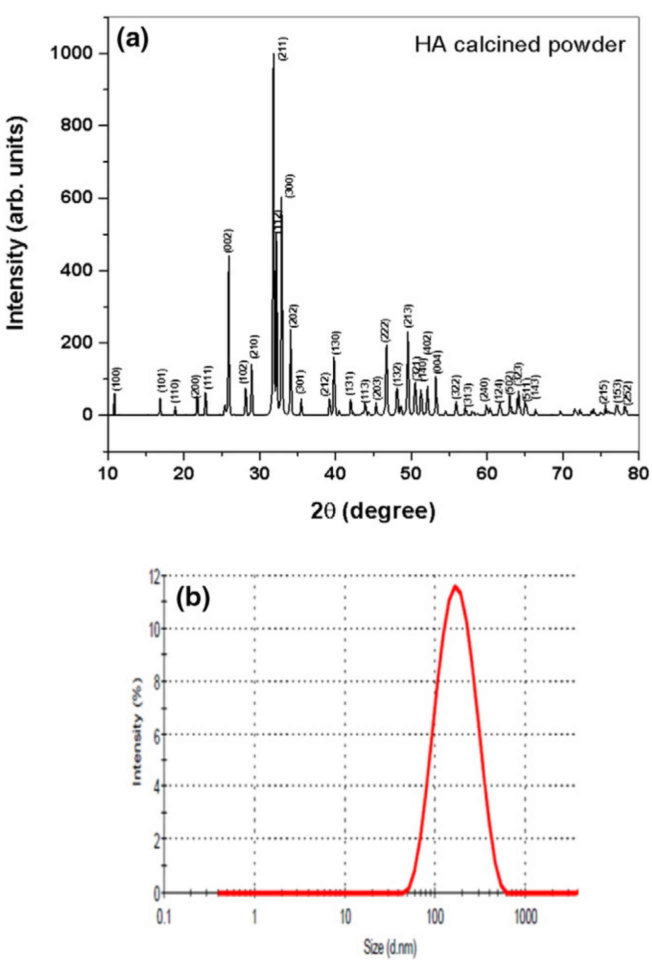

Fig. 2. (a) XRD pattern of HAp powder calcined at 600 °C/2 h (b) Particle size distribution of HAp powder.

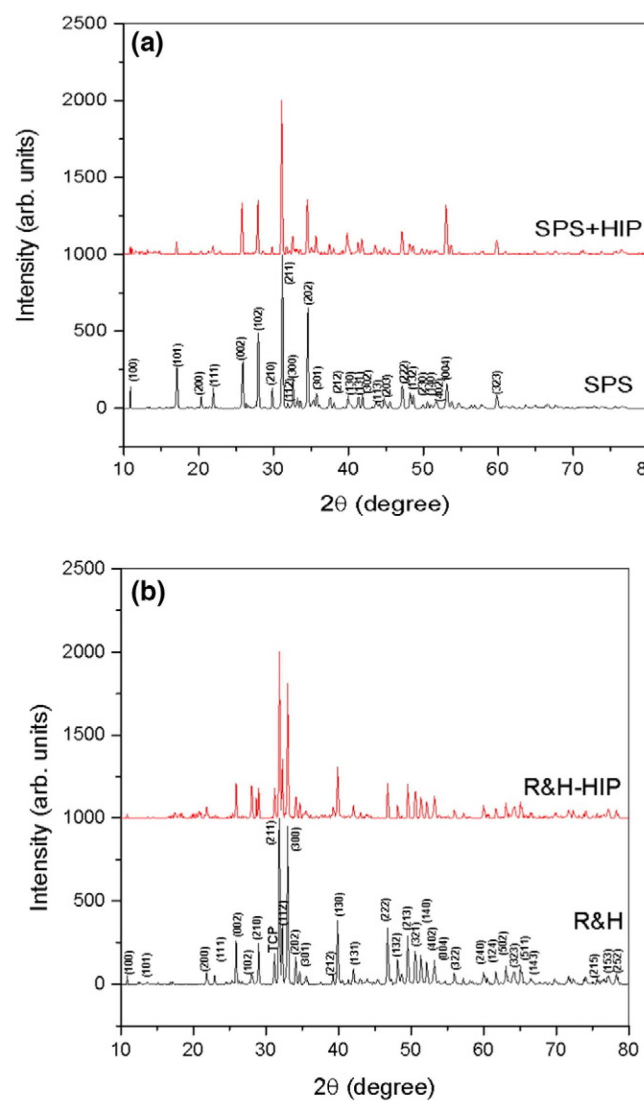

Fig. 3. (a) XRD patterns of hydroxyapatite SPS sintered at 900 °C/5 min (b) XRD patterns of hydroxyapatite R&H sintered at 1200 °C/90 min before and after HIP.