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Comparison of Electrical Properties between Ca and Sr Hydroxyapatites Materials.

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Abstract

Porous Calcium and Strontium hydroxyapatites (HAP) were prepared by wet chemical methods. The samples are characterized by XRD and SEM. Also electrical properties were measured at different relative humidity (RH). It is found that Sr-HAP is better dielectric material for bio-electronics application as it has higher dielectric constant than Ca-HAP. Dielectric constant of both the materials increases with RH due to the increase in polarizability of the structure. Conductivity was measured from impedance spectroscopy. Conductivity of both the materials increases with RH due to the increase in protonic conductor concentration. Intrinsic ionic conductivity in both the material decreases with the increase in temperature due to the loss of adsorb water in the lower temperature range.

Keywords: ceramics; hydroxyapatite; electrical properties; relative humidity;

1. INTRODUCTION

Ca-HAP ceramics are well-established as bio-compatible, bio-reactive, bio-ceramic materials [1]. They also possess other potential applications such as catalyst [2], sensor [3], ion-exchanger for harmful ion [4], electrolyte for high temperature fuel-cell [5] etc, because of there specific crystal structure. They have hexagonal crystal structure with large tunnels along c-axis, rendering a good diffusion of anionic species through the tunnels. Most of the above applications are related to the electrical properties of the apatite materials. Even natural bone shows a particular electrical pattern and that pattern is believed to have an influence on physiology, architecture and composition of living bone [6]. So a better knowledge of electrical conduction properties of apatite ceramics appears to be important to understand the electro-chemical and biological phenomena.

Small amount of Strontium (0.01-0.008%) [7] are frequently found in calcified tissues (bones and teeth). Strontium is similar to Calcium, so it can substitute for Ca in the matrix of bone relatively easily. In fact Strontium is often intentionally placed into bones of elderly people to relative some of the bone pain associated with cancer [8]. The electrical conductivity of hydroxyapatite ceramics is mainly related to the parameter such as polarizability and width of the channel, which are again related to the nature of metal cation around the channel of the HAP [9]. In the present work, a comparison of electrical properties between Ca-HAP and Sr-HAP is discussed. Conductivity measurements were carried out by complex impedance method at room temperature in two different relative humidity and at elevated temperature to understand the co-relation between different ionic conductivity in the apatite structure.

2. EXPERIMENTAL

Calcium and Strontium hydroxyapatite were prepared by mixing stoichiometric amounts of aqueous solutions of metal nitrate (Nice Chem., Chennai, >99%) and $(NH_4)H_2PO_4$ (Qualigens Chem, > 99%). The solutions were heated at 80°C under stirring condition and then the pH of the solution was adjusted to a value of 8 by the addition of ammonia solution. The resultant mixtures were aged for 24 hours. The precipitates were filtered and washed with water and IPA. Washed HAP's were dried in oven at 40°C. Dried powders were ground properly using pestle and mortar. The powders were uniaxially compressed at 5 tones into pellet samples. The pellets were sintered at 800°C. Phases of raw and calcined powders were identified by XRD (Phillips PW-1830, CuKα radiation with Ni-filter). For electrical measurements, silver electrodes were printed onto opposite sides of the pellets. Dielectric properties and electrical conductivity of Ca-HAP and Sr-Hap were measured using impedance method with a HP-4192A LF impedance analyzer in the frequency range 5Hz-13MHz. Experiments were performed at room temperature with two different humidity conditions and at elevated temperature also.

3. RESULTS AND DISCUSSION

It is known that apatites are stable at certain temperatures and that depends on the stoichiometry of the material. Fig.1. shows the X-ray diffraction patterns of raw and calcined powders of Ca, Sr-HAP. The Ca-HAP in the raw powder was indexed to match with PDF No. 46-0905, that is with $Ca_9(PO_4)_6H_2O$ and having Ca/P ratio 1.5. The Sr-HAP in the raw powder was indexed to match with PDF No. 33-1348, that is with $Sr_{10}(PO_4)_6(OH)_2$ .The lattice parameters were (a=9.4297 Å, c=6.8815 Å, for Ca-Hap) and (a=9.7703 Å, c=7.2816 Å, for Sr-Hap). So, Sr-HAP has bigger unit-cell then Sr-HAP as Sr^{+2} has higher ionic radius (1.13 Å) then Ca-HAP (0.99 Å). Upon calcination, at 900ºC both the HAP started decomposing into metal phosphate. That is why the two HAPs were sintered at 800°C.

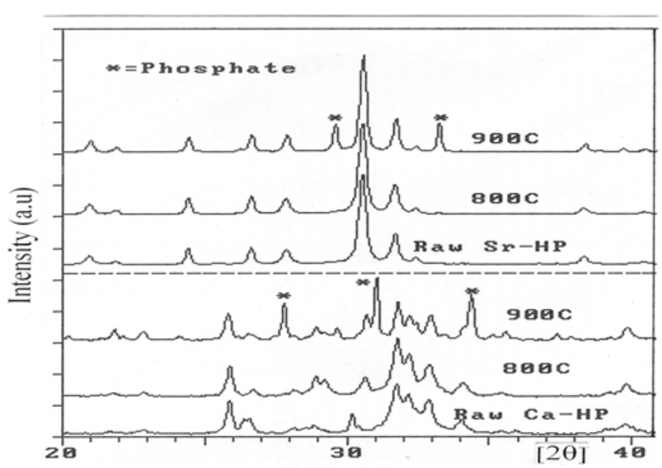

Figure 1. X.R.D of raw calcium HAP and strontium HAP

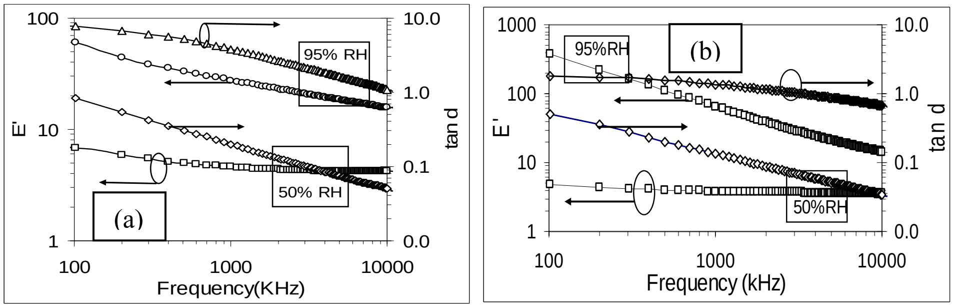

Figure 2. Frequency and humidity dependency of dielectric constant and loss for (a) Ca-HAP and (b) Sr-HAP.

Fig. 2 (a) and (b) shows the frequency dependency of dielectric constant (ε`) and dielectric loss (tan δ) for Ca-HAP and Sr-HAP samples at 50% and 95% relative humidity. It shows that dielectric constant as well as loss increases with the increase in humidity. Loss increases with the increase in H_2O, due to the increase in proton conductivity. But it is interesting to note that ε` increases with H_2O content, which indicate the increase in dielectric polarization due to the increase in polarizable ions and/or structural changes. Dielectric constants of both the materials are more or less stable in the 100 KHz to 10MHz range. Whereas dielectric losses are slightly dependent on frequency.

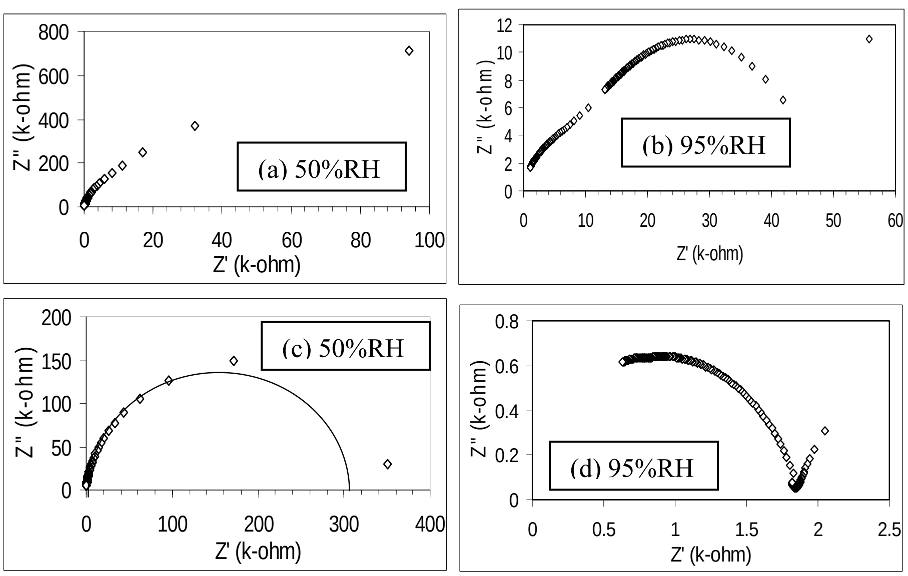

Figure 3. Complex impedance diagram for (a), (b) Ca-HAP and (c), (d) Sr-HAP at different humidifies.

Figure 3 shows complex impedance diagrams for Ca and Sr-HAP at 50% and 95% relative humidity. At 95% relative humidity, Ca-HAP exhibits 3 semi-circles in real (z') vs imaginary (z") impedance plot. Both Ca & Sr-HAP have higher conductivity at 90% RH than that of 50% RH. Bulk resistances were calculated from real axis intercepts of high frequency arc and were compared with the overall resistances calculated from dielectric constant and tan-δ. Bulk resistance for Ca-HAP were about $2*10^4$ and $1*10^4$ at 50% and 95% RH respectively, whereas the overall resistances calculated from dielectric constant were $1.4*10^6$ and $1.8*10^4$ respectively. Bulk resistances for Sr-HAP were about $3*10^5$ and $1.8*10^3$ at 50% and 95% RH respectively, whereas the overall resistances calculated from dielectric constant were $2.4*10^6$ and $1*10^4$

respectively. Overall resistances were higher due to the contribution from grain boundary resistances. Resistances decreases due to the change of RH from 50% to 95% for all the samples.

Arrhenius plots of the conductivity for Ca & Sr-HAP were ported in Figure 4. The conductivity of hydroxyapatites depends mainly on the nature of inserted cations. In fact, the high polarizability and the widening of tunnels by introducing the big cations favor the ionic conduction in Sr-Hap. Figure 5 shows that conductivity decreases with increase in temperature for both the apatites. For Ca-HAP, conductivity increases after 650°C. M. Sh. Khalil et.al[10] also reported the same behavior for calcium hydroxyapatite. The decrease in conductivity with increasing temperature may be due to the decreases in concentration of absorbed water molecules on the apatite materials with temperature. After 650°C, conductivity increases with temperature due to the increased release of thermally activated conducting ions from the structure. In case of strontium hydroxyapatite as we found that hydroxyapatite structure is very stable with strontium substitution release of mobile ions is difficult in the structure. Activation energy were calculated and compared for the two apatites in the descending region of Arrhenious plot. They are 0.71eV and 0.30eV for Ca & Sr-HAP respectively. Activation energy of calcium hydroxyapatite also calculated from ascending portion of Arrhenious curve and was found to be 0.51eV that is very much similar to its descending values of activation energy. It can be concluded from ionic conductivity measurements that calcium hydroxyapatite can be used as an ionic conductor in the temperature rang 650°C to 900°C, whereas strontium hydroxyapatite can be used at much higher temperature also i.e. greater than 1100°C.

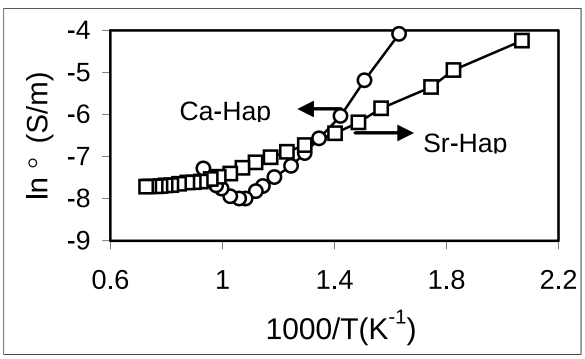

Fig.4. Arrhenius plots of the conductivity for Calcium and strontium hydroxyapatites.

4. CONCLUSIONS

It can be concluded that

1. Sr-HAP is better dielectric material for bio-electronics application as it has higher dielectric constant than Ca-HAP.
2. Dielectric constant of both the materials increases with RH due to the increase in polarizability of the structure.
3. Conductivity of both the materials increases with RH due to the increase in protonic conductor concentration.
4. Intrinsic ionic conductivity in both the material decreases with the increase in temperature due to the loss of adsorbs water in the lower temperature range and then increases due to increase in thermally activated protonic conductors.

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