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Dielectric properties of hydroxyapatite based Strontium doped powders produced by hydrothermal method

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Hydroxyapatite, one of the bioceramic materials, is one of the most biologically adaptable materials to the human body with the formula $Ca_{10}(PO_4)6(OH)_2$, which is similar to the structure of bone and tooth. For this HA is a biomaterial, HA was used in the study and pure HA and HA-based 1%, 5% and 10% Sr-doped nanopowders were produced and their FTIR-ATR, SEM and dielectric properties were examined. After FTIR-ATR analyzes taken from the produced powders confirmed that doping had occurred, the powders were turned into pellets and their dielectric properties were examined. It was determined that the materials were polarized in the frequency-dependent real and imaginary dielectric curves. The cole-cole and B(S)-G(S) curves examined later confirmed this situation. The change of the additive amount was examined by keeping the 10h reaction time and 180 °C temperature value constant. It has been observed that the polarization properties of the materials change depending on the amount of additives, therefore the produced materials can be used in biomedical applications.

Keywords: biomaterial, dielectric, hydroxyapatite, Strontium

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1. Introduction

The HA structure has a lattice of hydroxide ions located in the center of Ca^{2+} triangles along the c-axis of the hexagonal unit cell. OH- ions, together with Ca^{2+} and (PO_4^{-3}) ions, are aligned in columns parallel to the c-axis. Since hydroxyl ions in the C-axis pillars are thought to have an important role in ionic conduction, HA was considered as a one-dimensional anionic conductor (Gittings et al., 2008). There are various production methods to obtain hydroxyapatite. The hydrothermal method, which is a reliable, low-cost and practical method, was used in the study. [1-3].

Strontium (Sr) was used for doping in the study because its ions exhibit strong bone-like properties and properties similar to calcium, are not biologically harmful and are easily absorbed by bones. Sr decreases bone resorption by inhibiting osteoclast activity and improves bone formation by stimulating osteoblast activity. It is an element that can increase the bioactivity of biomaterials, especially in accelerating bone formation. In addition, research shows that the biological properties of Ca-P-containing materials are improved by the incorporation of Sr (Yong et al., 2018).

In this study, Hydroxiapatite (HA) and Sr doped HA were produced by hydrothermal method. Hydrothermal synthesis is a popular technique widely used in recent years in the production of materials with different chemical compositions. The hydrothermal method is generally based on the ability to dilute aqueous solutions of some insoluble substances such as oxides, sulfides and silicates under high pressure and temperature conditions. The properties of the products synthesized by hydrothermal method vary depending on the process kinetics of the synthesis. These parameters are the pH of the solution, the duration and temperature of the synthesis, the pressure of the system [4-9].

Therefore, the aim of this study is to investigate the effect of Sr doping on the physical, chemical and dielectric properties of HA based material by varying the doping rate at the same temperature and for the same time.

2. Experimental

Firstly, calcium nitrate tetrahydrate $Ca(NO_3)2.4H_2O$ and di-ammonium hydrogen phosphate $H_9N_2O_4P$ were used for the synthesis of pure HA. After these chemicals were dissolved separately in deionized water, the two solutions were brought together in a Teflon container, their pH was adjusted to 11 and then placed in the FYTRONIX FYHD-8000 hydrothermal system and the system was set to 180 ^oC for 10h and the reaction was started. After the reaction was finished and the system cooled down, the solution taken from the hydrothermal vessel was filtered on filter paper and dried on a hot plate at 50 ^oC for 3 days. To prepare Sr-doped samples, Sr-doped HA powders were produced under the same conditions by increasing the mole ratio of Stransium in response to calcium deficiency so that the Ca/P ratio of 1.67 of hydroxyapatite was maintained. These processes were repeated for 1%, 5% and 10% Sr doped nanopowders. The resulting pure HA and Sr-doped HA nanopowders were pressed into round pellets under a pressure of 5 tons.

While ATR-FTIR and SEM analyses were performed from the produced nanopowders, the dielectric properties of the biomaterials from the produced pellets were analyzed.

Figure 1 shows the reaction process of biomaterials produced by hydrothermal method.

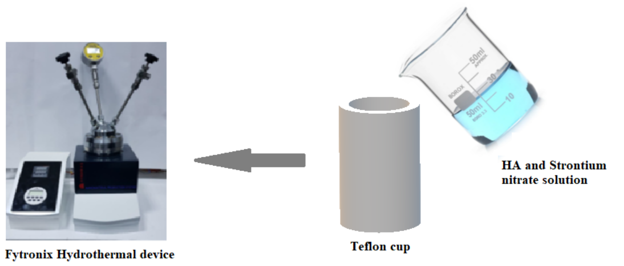


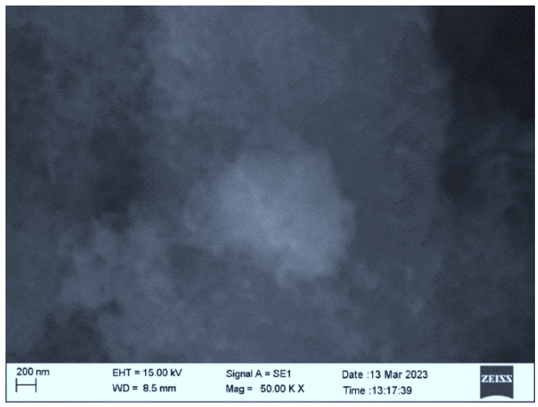
Figure 1: Hydrothermal synthesis stage.

In figure 2 shows the measurement process of pelletized HA-based biomaterials on a two-probe fytronix holder. While the lower contact probe was in contact with the holder, a metal upper contact of the same diameter was placed on the pelletized biomaterial and the dielectric analysis of the biomaterials was performed after the upper probe was in contact with the metal contact.

Figure 2: Fytronix sample holder

3. Results

According to the SEM analysis given in Figure 3 a), b),c), d), although no significant change was observed depending on the amount of additive in pure HA and 1%, 5% and 10% Sr doped HA samples, it was observed that there were more cracks on the surface in the 10% Sr doped HA sample. Cracks in the structure may result from the applied pressure and internal residual stress.



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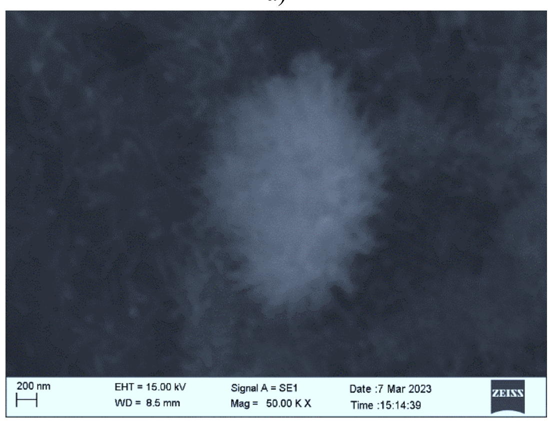

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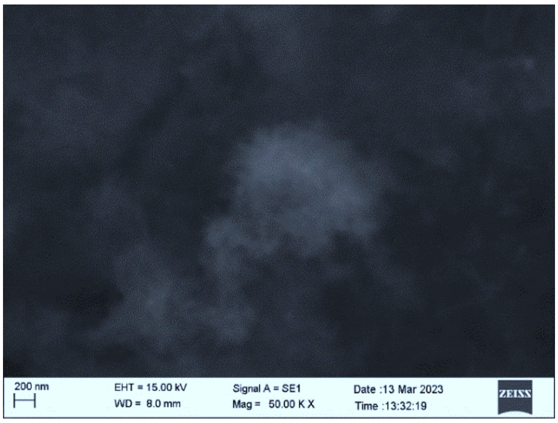

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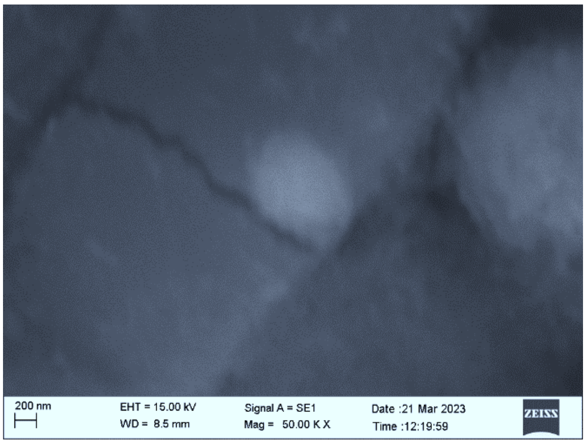
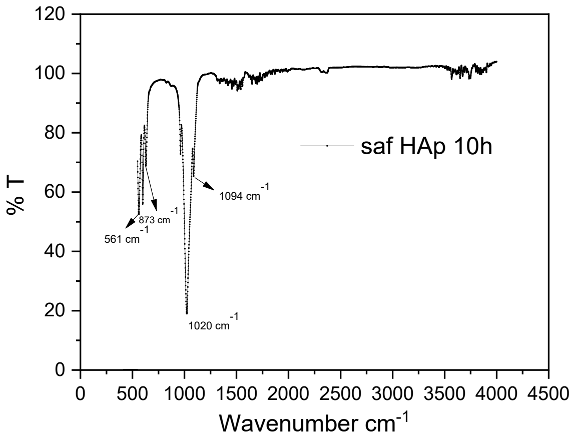


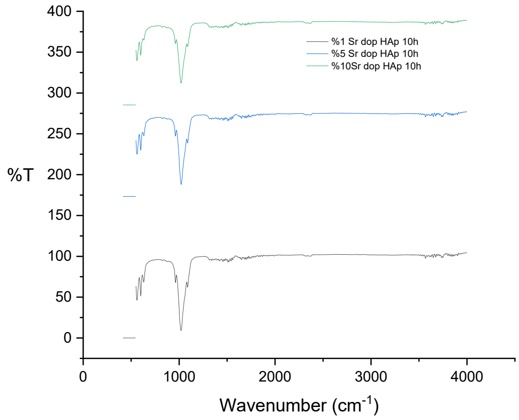
d)

Figure 3: SEM photographs of biomaterial hydrothermally produced with a) pure HA b) %1 Sr doped HA c) %5 Sr doped HA d) %10 Sr doped HA 10h coating (50000x)

Fourier transform infrared spectroscopy - attenuated total reflection (FTIR-ATR) was used to analyze the chemical structures and specific functional groups of the biomaterials produced. As seen in Figure 4, while there is a very small change in the positions of the peaks depending on the amount of additive, significant changes in the peak intensities are observed.



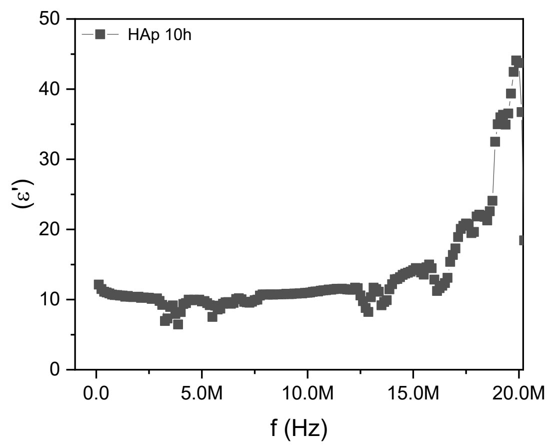
a)



b)

Figure 4: ATR-FTIR analysis of a) pure HA and b) 1%, 5%, 10%, Sr doped HA powder samples at 10h reaction time

Dielectric spectroscopy is a form of impedance spectroscopy in which the dielectric properties of biomaterials (dielectric constant and dissipation factor, capacitance, conductivity, etc.) are characterized as a function of frequency. Dielectric spectroscopy (DS) is a form of impedance spectroscopy. DS can provide important information about the dynamic and structural properties of substances. It is particularly sensitive to intermolecular interactions and has the ability to monitor various processes. In the real dielectric constant curves seen in Figure 5. a) and b) an increase, that is, a change, in the dielectric constant (ε'-frequency) was observed after a certain frequency value. This change in dielectric constant indicates that the produced biomaterials have the ability to be polarized. Therefore, it was concluded that the materials we produced can be used in biomedical applications.



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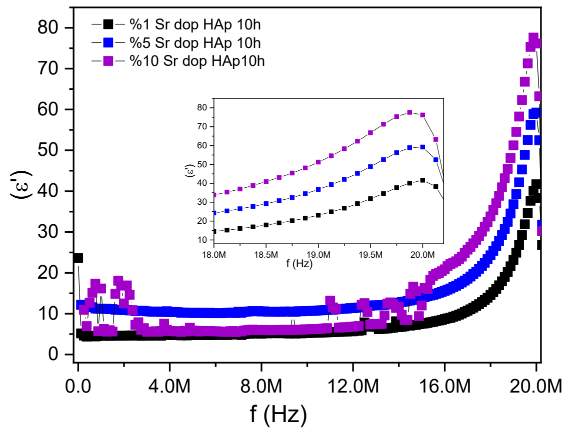
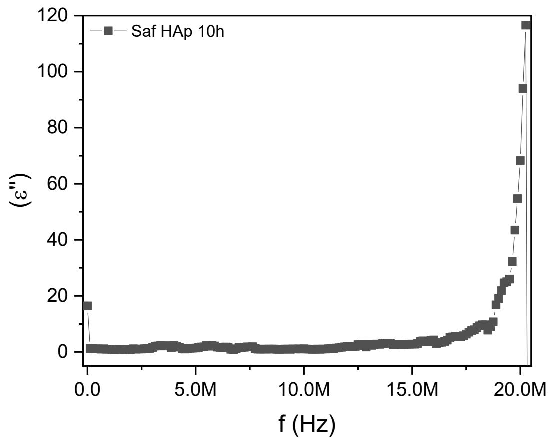


b)

Figure 5: Dielectric constant of a) pure HA and b) %1, %5,%10 Sr-doped HA.

The loss dielectric constant (ε″-frequency) curves of pure HA and Sr doped HA based pelletized powder samples with 1%, 5% and 10% Sr doping are shown in Figure 6.a) and b). No significant change was observed in the dielectric loss factor depending on the doping amount.



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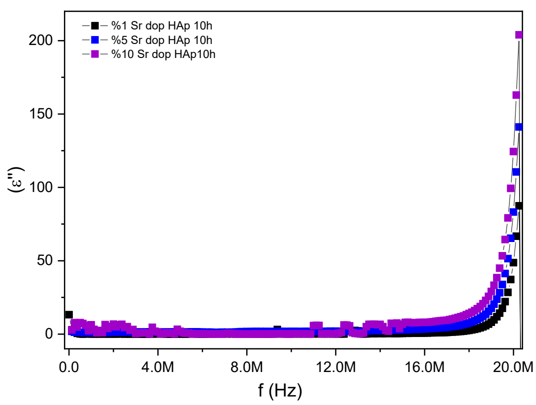
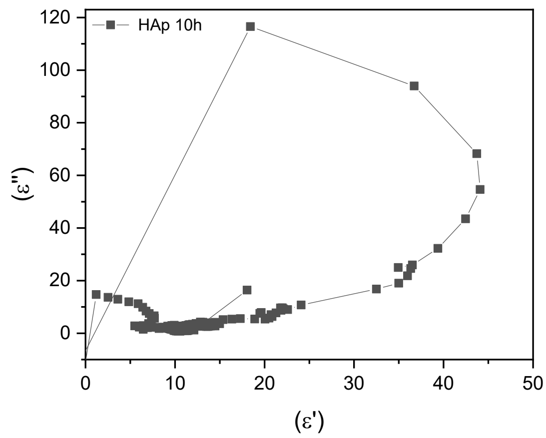


b)

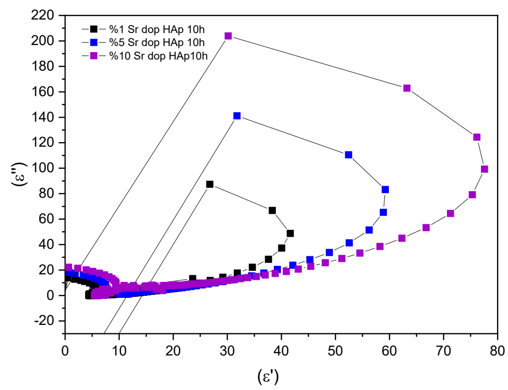
Figure 6: Dielectric loss factor of a) pure HA and b) %1, %5,%10 Sr-doped HA.

The cole-cole curves of pure HA and %1, %5,%10 Sr-doped HA pelletized powder samples are shown in Figure 7. a) and b). The Cole cole curve is the measure of the change in the dielectric dipole moment. In other words, it causes a change in the relative permeability and dielectric loss values.

The values of Ɛ' and Ɛ″ are extremely important in defining the properties of the dielectric material. As the amount of additive increased, a greater increase in the diameter of the cole-cole curve was observed. Dielectric materials with a single relaxation time comply with the Debye model. In dielectric materials with multiple relaxation times, a semicircle or an arc is formed whose center lies below the Ɛ″= 0 axis (Balcı 2021). The curves in Figure 7 are generally not Debye type.



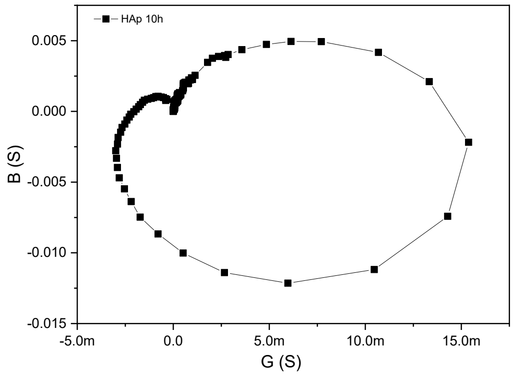
a)



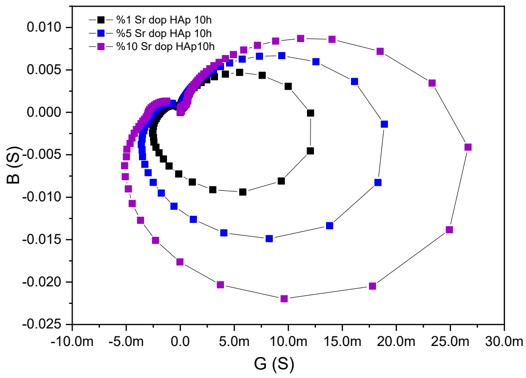
b)

Figure 7: The cole-cole curve of a) pure HA and b) %1, %5,%10 Sr-doped HA

Figure 8 shows the B(S)-G(S) curves of pure HA and %1, %5,%10 Sr-doped HA pelletized powder samples at 10h growth temperature. B(S)-G(S), that is, cole-cole curves of impedance. When the diameters of the impedance-dependent cole-cole curves were examined, it was observed that they had non-Debye type behavior. While the diameter of pure HA was small, the diameter values increased depending on the amount of doping, indicating that polarization increased with doping and the samples could be used in biomedical applications.



a)



b)

Figure 8: B(S)-G(S) curves of a) pure HA and b) %1, %5,%10 Sr-doped HA

4. Conclusion

As a result, FTIR-ATR results of pure HA and 1%, 5% and 10% Sr doped HA biomaterials produced by the hydrothermal method, which is an easy and cheap method, showed that doping occurred and according to dielectric analysis, the produced materials were polarized.

It has been determined that a change in dielectric, that is, polarization properties, is observed depending on the doping amounts, and therefore the produced materials can be used in biomedical applications.

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